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**Cooper et al.**

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(54) **METHOD FOR IMPROVING TOTAL ENERGY DEMAND IN A POST-COMBUSTION CARBON CAPTURE PROCESS WITH IONIC ABSORBENT**

(58) **Field of Classification Search**

None

See application file for complete search history.

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(\*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 920 days.

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(52) **U.S. Cl.**

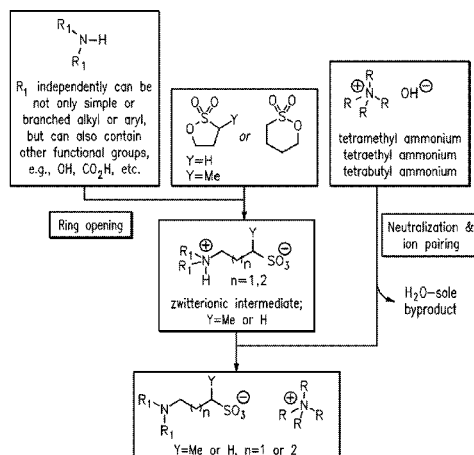
CPC ..... **B01D 53/1493** (2013.01); **B01D 53/1475** (2013.01); **B01D 53/62** (2013.01);

(Continued)

(57) **ABSTRACT**

Disclosed herein is a method for improving the total energy demand required to separate carbon dioxide (CO<sub>2</sub>) from an aqueous ionic absorbent solution in a post-combustion carbon capture process. The method involves (a) contacting a flue gas stream containing CO<sub>2</sub> with an aqueous ionic absorbent solution under absorption conditions to absorb at least a portion of the CO<sub>2</sub> from the flue gas stream and form a CO<sub>2</sub>-aqueous ionic absorbent solution stream, wherein the aqueous ionic absorbent solution comprises one or more diluents and an ionic absorbent containing a cation and an anion comprising an amine moiety; and (b) subjecting at least a portion of the CO<sub>2</sub>-aqueous ionic absorbent solution stream to desorption conditions to form a CO<sub>2</sub>-rich stream and an aqueous ionic absorbent solution stream having a reduced CO<sub>2</sub> content.

**14 Claims, 9 Drawing Sheets**



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*C07C 323/25* (2006.01)  
*B01D 53/78* (2006.01)  
*B01D 53/96* (2006.01)  
*B01D 53/14* (2006.01)

(52) **U.S. Cl.**

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*2252/20405* (2013.01); *B01D 2252/20426*  
(2013.01); *B01D 2252/30* (2013.01); *B01D*  
*2258/0283* (2013.01); *Y02C 10/04* (2013.01);  
*Y02C 10/06* (2013.01); *Y02C 10/08* (2013.01)

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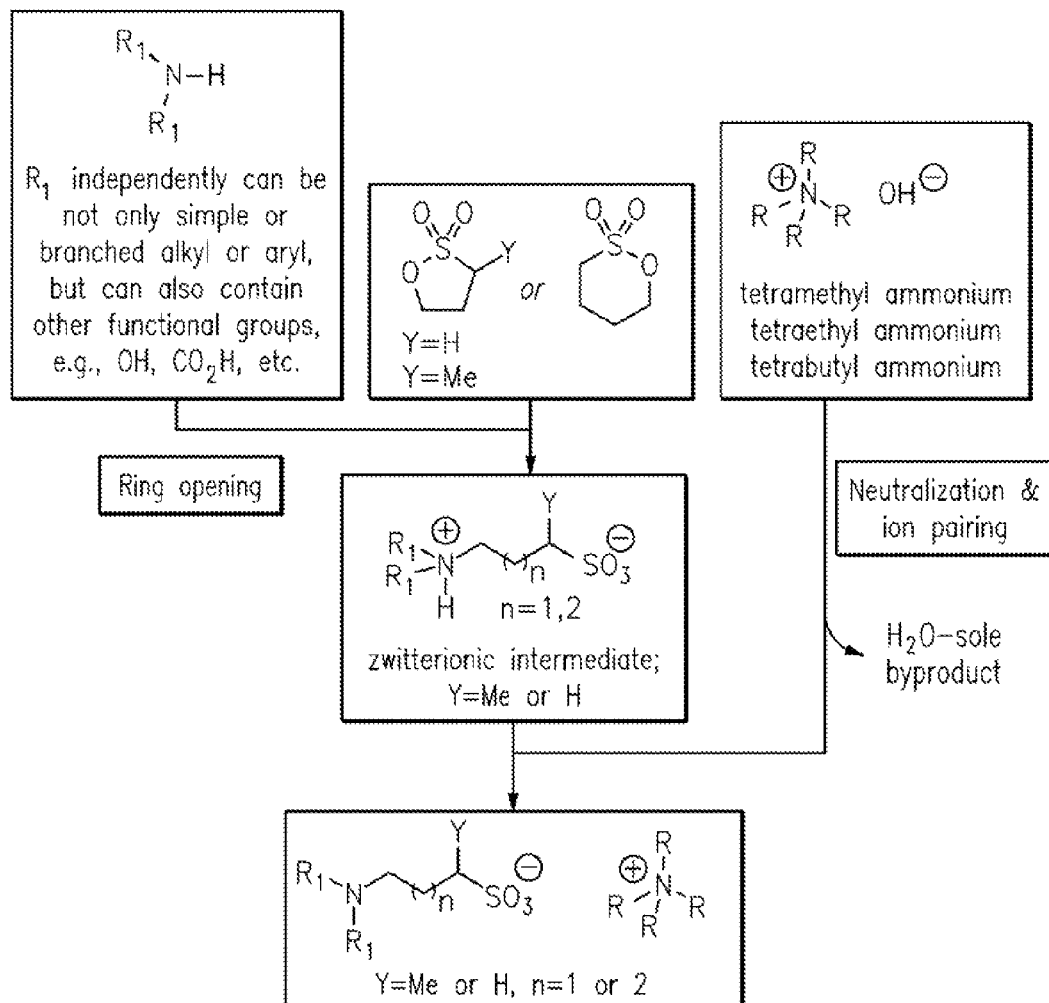


FIG. 1

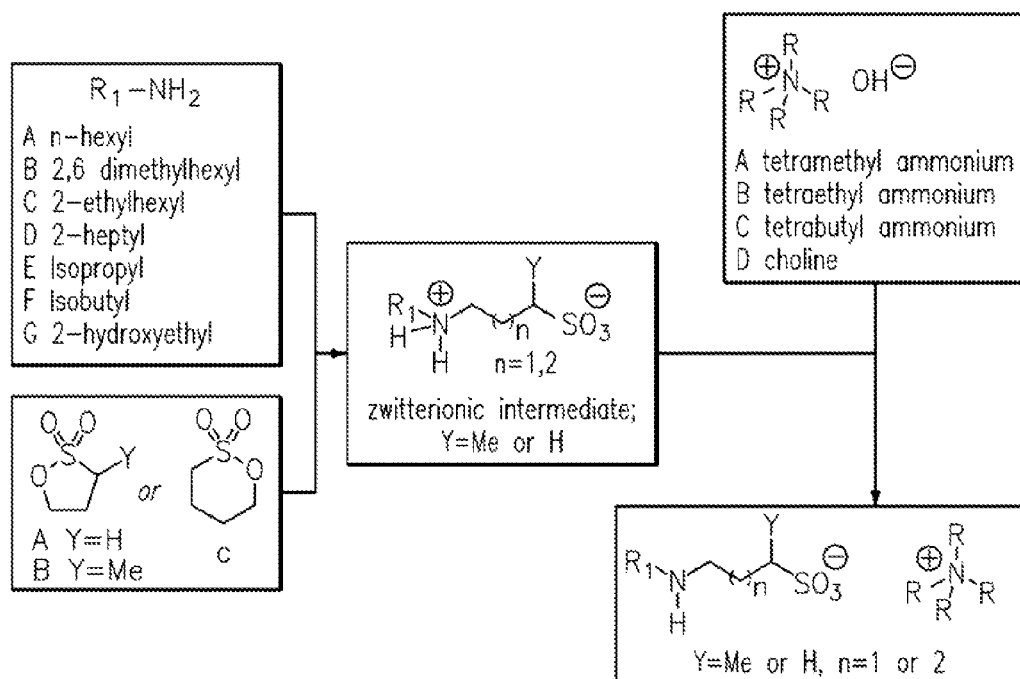


FIG. 2

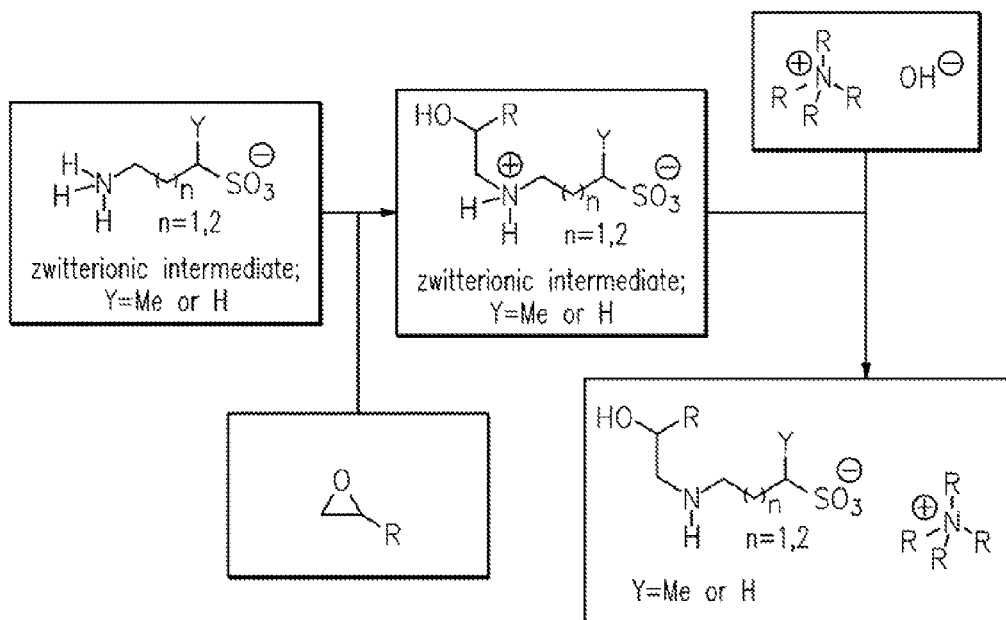


FIG. 3

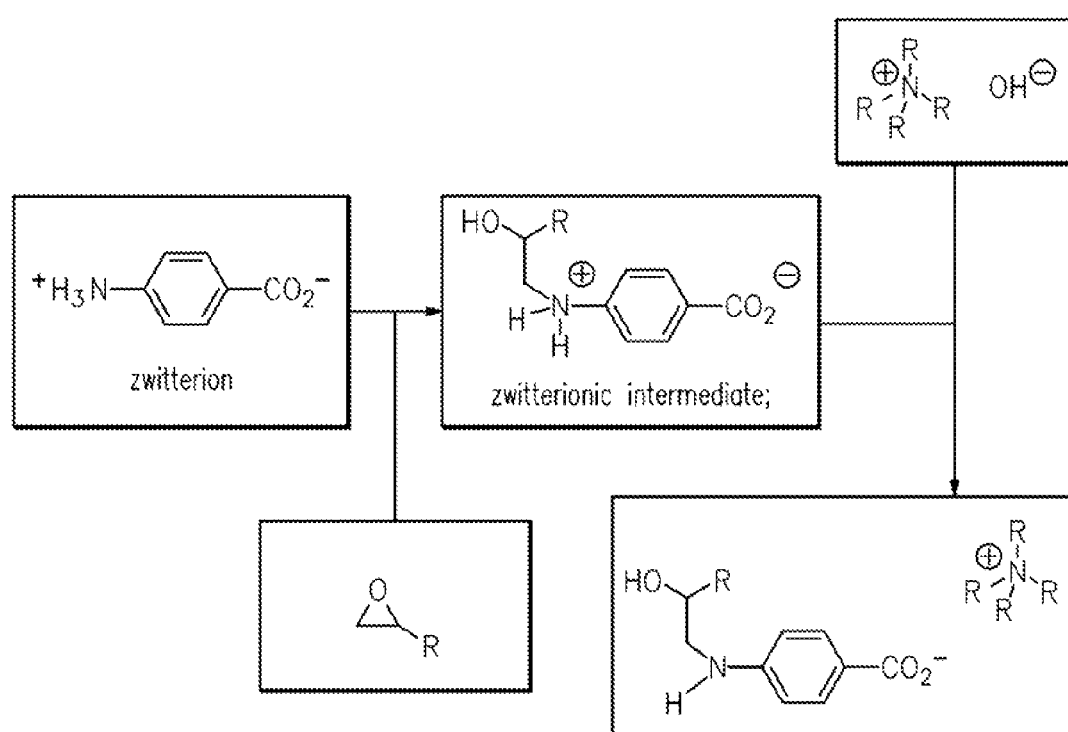


FIG. 4

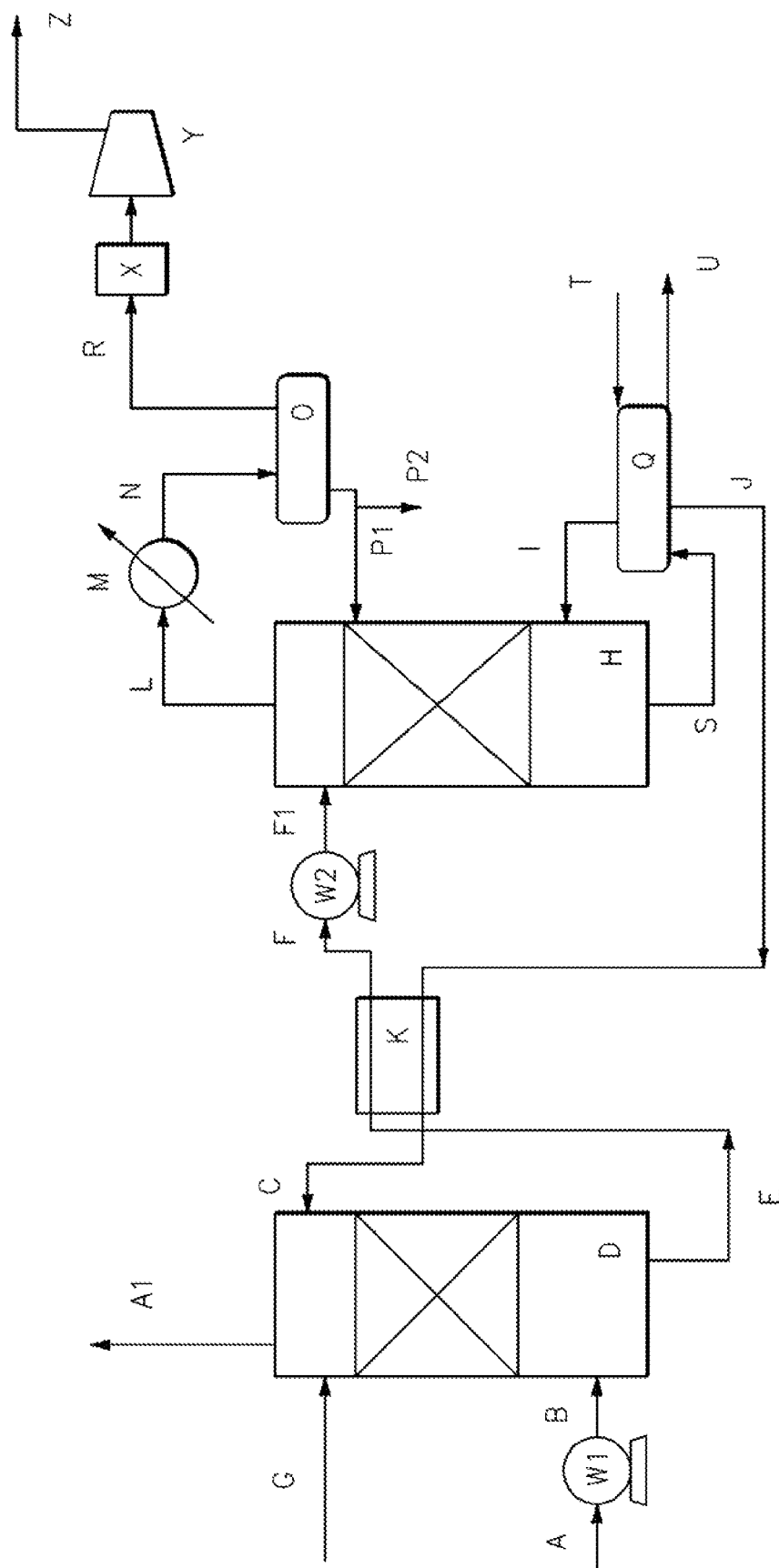


FIG. 5

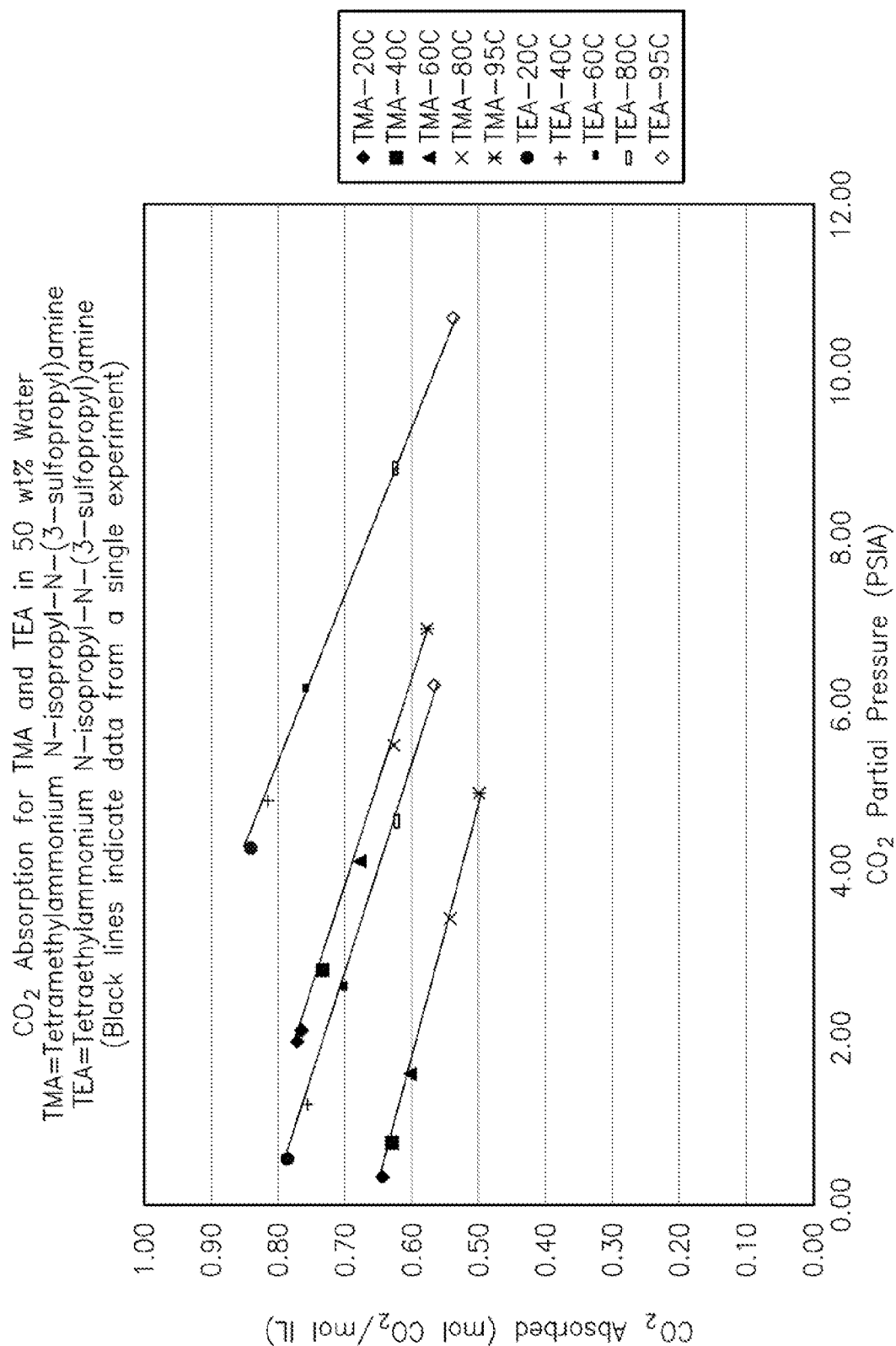


FIG. 6

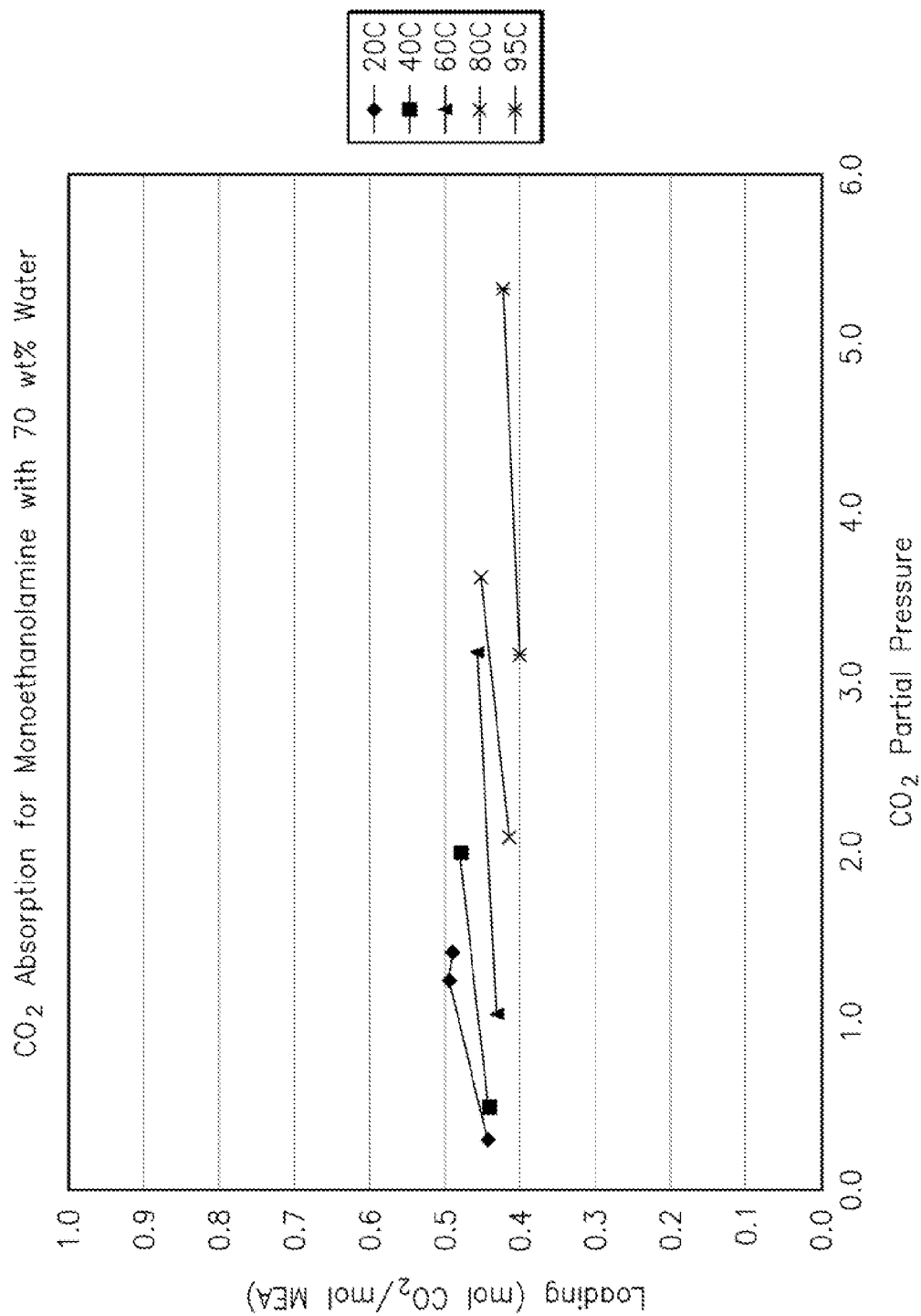


FIG. 7



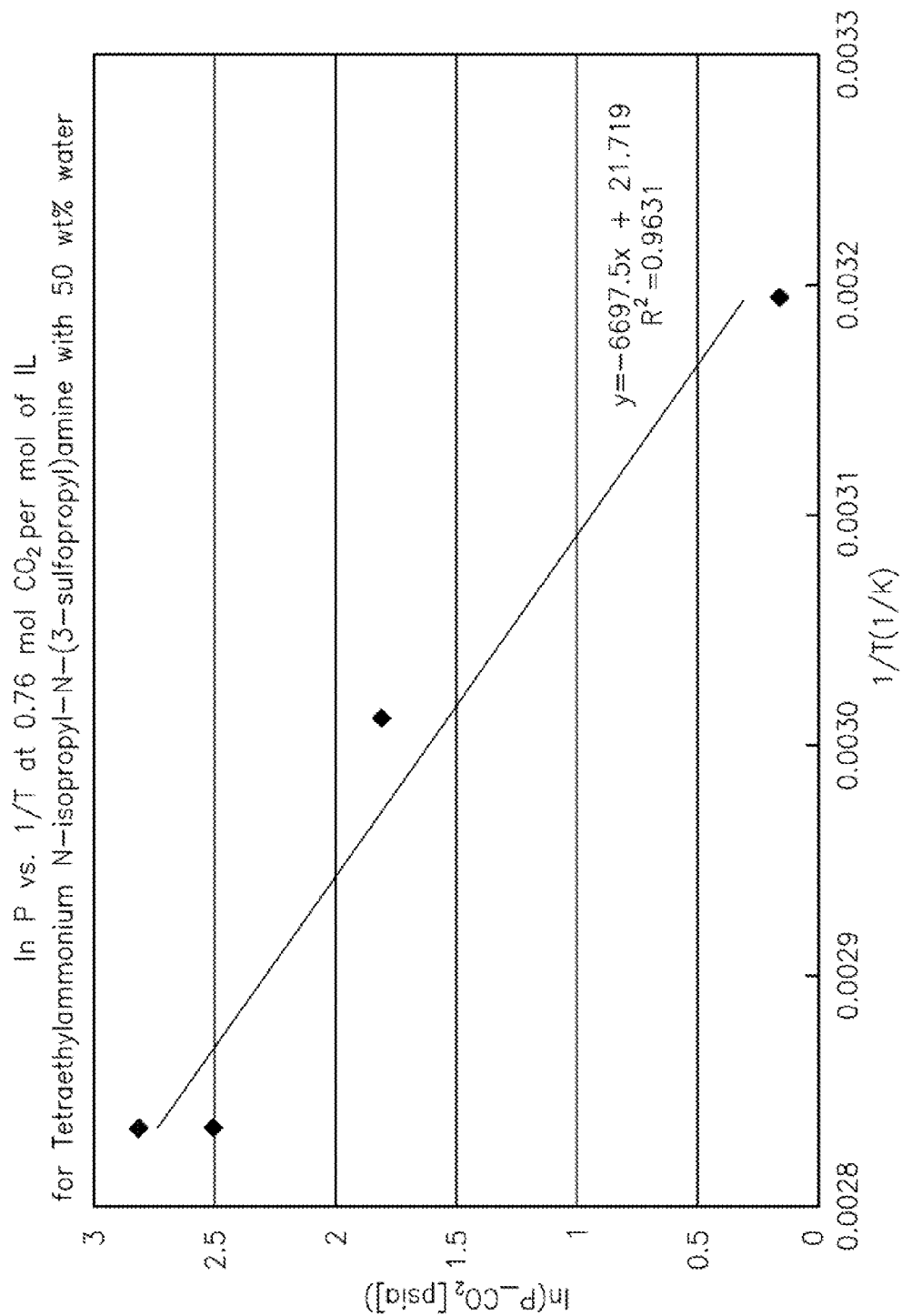


FIG. 8

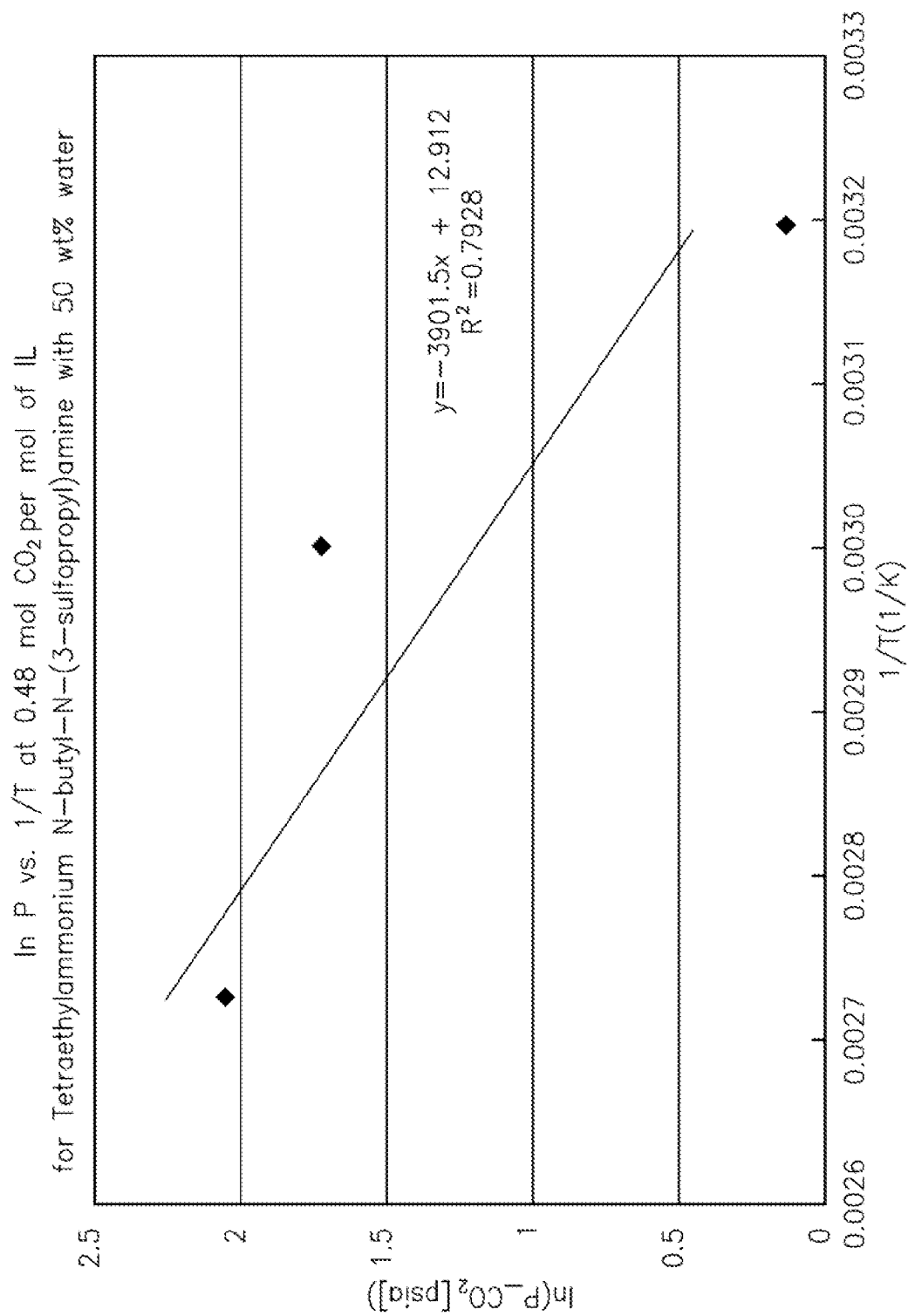


FIG. 9

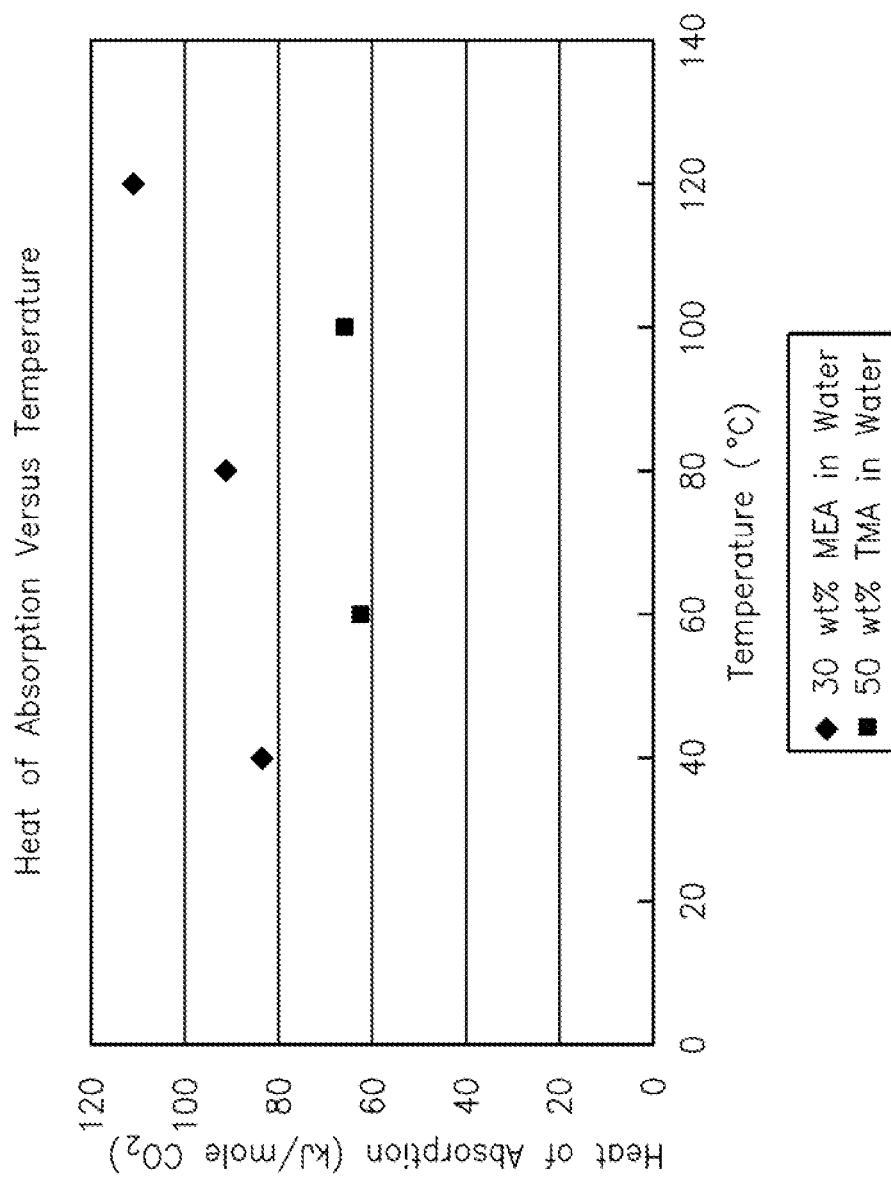


FIG. 10

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# METHOD FOR IMPROVING TOTAL ENERGY DEMAND IN A POST-COMBUSTION CARBON CAPTURE PROCESS WITH IONIC ABSORBENT

## PRIORITY

This application claims the benefit under 35 U.S.C. § 119(e) to U.S. Provisional Application No. 61/460,336, filed Dec. 30, 2010, the contents of which are incorporated by reference herein.

## BACKGROUND

### 1. Technical Field

The present invention generally relates to method for improving the total energy demand required to separate carbon dioxide from an aqueous ionic absorbent solution in a post-combustion carbon capture process.

### 2. Description of the Related Art

The removal of carbon dioxide from natural gas is commercially practiced now in order to obtain natural gas, which satisfies sales specifications or other process-dependent requirements. Carbon dioxide is one of the primary combustion products as fuel is burned and is emitted into the atmosphere as a waste flow in the flue gas. Removal of carbon dioxide from the flue gas is not commonly practiced at the present time. As the efforts to control CO<sub>2</sub> emissions into the atmosphere increase, the removal of carbon dioxide from flue gas may become necessary at an industrial scale in order to satisfy carbon dioxide emission requirements which may be set by air pollution control authorities. The CO<sub>2</sub> removal process from natural gas may not be directly applied to the CO<sub>2</sub> removal from flue gas since the conditions of these two processes are very different. The process of CO<sub>2</sub> removal from flue gas and then recovery of CO<sub>2</sub> is generally called a post-combustion carbon capture process. One of the more promising post-combustion carbon capture processes utilizes an absorbent solution to remove CO<sub>2</sub> from the flue gas and then recovers CO<sub>2</sub> from the absorbent solution.

Several processes for removing carbon dioxide from gases are known. Examples of such processes for carbon dioxide separation and capture include chemical absorption, physical and chemical adsorption, low-temperature distillation, gas-separation membranes, mineralization/biomineralization, and vegetation. The carbon dioxide absorption process is a unit operation where one or more components in a gas mixture are dissolved in a liquid (solvent). The absorption may either be a purely physical phenomenon or involve a chemical reaction, such as the reaction between carbon dioxide and an amine. Generally, the liquid solvent is an aqueous amine solution for the removal of carbon dioxide from gas streams.

An example of an absorption process is the process for removing carbon dioxide from flue gas by means of monoethanolamine (MEA) or diethanolamine (DEA). The flue gas is led into an absorption column where it comes into contact with MEA or DEA which absorbs the carbon dioxide molecules. Typically, these amines, MEA and DEA, are used as 25 to 30 wt. % amine in an aqueous solution. The amine solution enters the top of an absorption tower while the carbon dioxide containing gaseous stream is introduced at the bottom. The solvent is then led to a desorption process where the liquid is heated, and the carbon dioxide molecules are removed from the solvent by means of a desorption column. Carbon dioxide and water emerge from the amine solution and the water is separated by condensing the water vapor in a

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heat exchanger. The solvent is cooled and then recycled back, to the absorption tower for additional carbon dioxide absorption.

Solvent chemistry, corrosion, and viscosity considerations limit the amine strength to about 30 wt. % MEA. At flue-gas carbon dioxide partial pressures (e.g., 0.04 to 0.15 atm), the carbon dioxide-rich ("rich") solvent loading is about 0.42 to 0.45 mol CO<sub>2</sub>/mol MEA and the CO<sub>2</sub>-lean ("lean") solvent loading is about 0.15 to 0.17 mol CO<sub>2</sub>/mol MEA. The difference in loading (0.25 to 0.3 mol CO<sub>2</sub>/mol MEA) sets the circulation rate of the amine and influences capital and operating costs.

MEA also has disadvantages in that it has several mechanisms of loss, and a continuous makeup of MEA is required for a flue gas CO<sub>2</sub> removal process or post-combustion carbon capture process. For example, MEA degrades in the presence of oxygen from the flue gas. Thus, to limit the oxidative degradation, corrosion inhibitors may be used. MEA also degrades into heat-stable salts (HSS) from reaction with carbon dioxide. To solve this problem, a reclaiming would be added on the regenerator to separate the HSS from the amine solution to provide suitable makeup MEA. Lastly, the volatility of MEA results in the treated flue gas containing in excess of 500 ppmv MEA when leaving the absorber to the vent. To address this, a wash section is added at the top of the absorber and makeup water is added to scrub the MEA from the treated flue gas. The mixture is then sent down the column along with the remaining lean solvent to absorb carbon dioxide from the incoming flue gas. Water washing can cut the MEA emissions to about 3 ppmv.

MEA may also degrade over time thermally, thereby limiting the temperature of operation in the absorber and regenerator. With a cooled flue gas inlet temperature of about 56° C., the absorber column may operate at a bottoms temperature of 54° C. and a pressure of 1.1 bar while the regenerator may operate at a bottoms temperature of 121° C. (2 bar saturated steam) at 1.9 bar. For 30 wt. % MEA, the amine reboiler steam temperature is kept at less than 150° C. (4.7 bar saturated steam) to limit thermal degradation.

MEA also degrades in the presence of high levels of NO<sub>x</sub> and SO<sub>x</sub> which are common in facilities that burn coal and fuel oil. However, if carbon dioxide removal from a high NO<sub>x</sub> and SO<sub>x</sub> containing flue gas is desired, separate process facilities such as SCR (Selective Catalytic Reduction) and FGD (Flue Gas Desulfurization) are needed for removal of NO<sub>x</sub> and SO<sub>x</sub>, respectively.

Other drawbacks with amine solutions such as MEA and DEA are 1. Intensive energy requirements: During the regeneration step, heating energy is required to break the chemical bonds between the absorbed CO<sub>2</sub> and solvent. Energy is also required to generate steam within the amine regenerator to strip the CO<sub>2</sub> from the solvent. For some particularly strongly-absorbing amines (e.g., MEA) and for large, circulation rates, this energy requirement can be very high and represents a significant operating expense. Due to the high energy requirements, CO<sub>2</sub>-rich amine solutions are only partially regenerated to a lower CO<sub>2</sub> loading (CO<sub>2</sub>-lean state) during the regeneration step.

Another disadvantage with the use of MEA is the solution of 30 wt. % MEA in water has a relatively high heat of absorption for CO<sub>2</sub>, i.e., a heat of absorption of 82 kJ/mol of CO<sub>2</sub>. Solvents with a high heat of absorption will further result in an increased energy demand for stripping CO<sub>2</sub> from the loaded MEA solution.

The total energy demand is an important parameter for estimating the cost of operating the post-combustion flue gas carbon capture process as well as a measure of the perfor-

mance and viability of the absorption solvent. Accordingly, an increase in the total energy demand for stripping CO<sub>2</sub> from the absorption solvent will result in an increase in the operating cost for the post-combustion capture process.

Because of the significant costs involved, proper amine selection for the absorption solvent requires careful evaluation of these factors for the specific application since the criticality of these factors varies for different amines. In other words, one faces a trade-off and optimization between benefits and costs. Nevertheless, in general, the main disadvantage for amine-based CO<sub>2</sub> removal processes remains the high energy consumption requirements.

Accordingly, in order to have an improved, low cost, post-combustion carbon dioxide removal technology that is better than those known in the art (i.e., 30 wt. % MEA and similar aqueous amines), it is desirable to develop a method for improving the total energy demand required to separate carbon dioxide (CO<sub>2</sub>) from an aqueous absorbent solution (i.e., stripping (or solvent regeneration)) in a post-combustion carbon capture process.

### SUMMARY

In accordance with one embodiment of the present invention, there is provided a method for improving the total energy demand required for a post-combustion carbon capture process to capture carbon dioxide (CO<sub>2</sub>) from flue gas, the method comprising (a) contacting a flue gas stream containing CO<sub>2</sub> with an aqueous ionic absorbent solution having a heat of absorption of about 20 to no more than about 70 kJ/mol of CO<sub>2</sub> under absorption conditions to absorb at least a portion of the CO<sub>2</sub> from the flue gas stream and form a CO<sub>2</sub>-aqueous ionic absorbent solution stream; and (b) subjecting at least a portion of the CO<sub>2</sub>-aqueous ionic absorbent solution stream to desorption conditions to form a CO<sub>2</sub>-rich stream and an aqueous ionic absorbent solution stream having a reduced CO<sub>2</sub> content.

In accordance with a second embodiment of the present invention, there is provided a method for improving the total energy demand required to separate carbon dioxide (CO<sub>2</sub>) from an aqueous ionic absorbent solution in a post-combustion carbon capture process, the method comprising (a) contacting a flue gas stream containing CO<sub>2</sub> with an aqueous ionic absorbent solution under absorption conditions to absorb at least a portion of the CO<sub>2</sub> from the flue gas stream and form a CO<sub>2</sub>-aqueous ionic absorbent solution stream, wherein the aqueous ionic absorbent solution comprises one or more diluents and an ionic absorbent containing a cation and an anion comprising an amine moiety; and (b) subjecting at least a portion of the CO<sub>2</sub>-aqueous ionic absorbent solution stream to desorption conditions to form a CO<sub>2</sub>-rich stream and an aqueous ionic absorbent solution stream having a reduced CO<sub>2</sub> content.

The present invention advantageously provides methods for improving the total energy demand required to separate carbon dioxide (CO<sub>2</sub>) from an aqueous ionic absorbent solution in a post-combustion carbon capture process. By employing an ionic absorbent containing a cation and an anion comprising an amine moiety in the aqueous ionic absorbent solution, a more efficient CO<sub>2</sub> capture process can be achieved while lowering the operating costs to separate the CO<sub>2</sub> from the aqueous ionic absorption solution. The ionic absorbent employed in the method of the invention can be operated in a wide range of temperatures and pressures. Thus, the CO<sub>2</sub> capturing process conditions can be chosen to increase the loading difference between the "rich" and "lean" CO<sub>2</sub> capacities.

As one skilled in the art will readily appreciate, the chemical absorption capacity of solvents decreases with (1) decreasing partial pressure of the absorbed species in the gas phase and (2) increasing temperature. Accordingly, the ionic absorbent employed in the methods of the present invention can be diluted with a sufficient amount of solvent to adjust the viscosity and improve the absorption or desorption rate. Therefore, by adjusting the absorption and stripping process conditions, such as temperatures, pressures and concentration of ionic absorbent in the solution, one can further optimize the total energy demand required for post-combustion carbon capture process using the ionic absorbent disclosed herein.

### BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1-4 shows generic synthetic schemes for preparing an ionic absorbent in accordance with the present invention.

FIG. 5 shows a process flow diagram scheme for the removal of CO<sub>2</sub> from a flue gas stream in accordance with one embodiment of the present invention.

FIG. 6 shows the CO<sub>2</sub> loading results at various temperature for amine-functionalized ionic absorbents in accordance with the present invention.

FIG. 7 shows the CO<sub>2</sub> loading results at various temperature for monoethanolamine in 70 wt. % water.

FIG. 8 shows a graph for estimating the heat of absorption for tetraethylammonium N-isopropyl-N-(3-sulfopropyl) amine (TEA).

FIG. 9 shows a graph for estimating the heat of absorption for tetraethylammonium N-butyl-N-(3-sulfopropyl)amine.

FIG. 10 shows a plot of the heat of absorption of CO<sub>2</sub> in aqueous solutions of monoethanolamine (MEA) and tetraethylammonium N-isopropyl-N-(3-sulfopropyl)amine (TMA) as a function of temperature.

### DETAILED DESCRIPTION

In one embodiment, the present invention is directed to a method for improving the total energy demand required to separate carbon dioxide (CO<sub>2</sub>) from an aqueous ionic absorption solution. In general, the method involves (a) contacting a gas stream containing CO<sub>2</sub> with an aqueous ionic absorbent solution having a heat of absorption of about 20 to no more than about 70 kJ/mol of CO<sub>2</sub> under absorption conditions to absorb at least a portion of the CO<sub>2</sub> from the gas stream and form a CO<sub>2</sub>-aqueous ionic absorbent solution stream; and (b) subjecting at least a portion of the CO<sub>2</sub>-aqueous ionic absorbent solution stream to desorption conditions to form a CO<sub>2</sub>-rich stream and an aqueous ionic absorbent solution stream having a reduced CO<sub>2</sub> content.

The flue gas stream for use in the process of the present invention may be any flue gas stream that is generated from a combustion apparatus such as a refinery plant, industrial power plant, etc. In one embodiment, the flue gas stream is from a stack that removes flue gas discharged from an industrial facility to the outside. Representative examples of such flue gas streams includes a gas turbine flue gas, a furnace flue gas, a hot oil furnace flue gas, a steam generator flue gas, a preheater flue gas, a reformer flue gas, steam methane reformer flue gas, FCC (fluid catalytic cracker) regenerator flue gas, CFB (circulating fluid bed boiler) and the like. The flue gas stream contains at least some amount of water vapor and CO<sub>2</sub>. In one embodiment, the flue gas stream is fully saturated with water. In another embodiment, the flue gas stream contains about 50% up to 100% humidity.

In general, the amount of CO<sub>2</sub> present in the flue gas will depend from its source. For example, for a flue gas from a

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combined cycle gas turbine, the flue gas stream contains about 3.5 mol % CO<sub>2</sub>. Alternatively, for a flue gas from steel production or cement kilns, the flue gas stream contains about 30 mol % CO<sub>2</sub>. Accordingly, in one embodiment, the flue gas stream contains from about 3.5 mol % to about 30 mol % CO<sub>2</sub>. In another embodiment, the flue gas stream contains from about 4 mol % to about 15 mol % CO<sub>2</sub>. In another embodiment, the flue gas stream contains from about 10 mol % to about 15 mol % CO<sub>2</sub>.

In general, the flue gas stream is typically a hot flue gas stream, i.e., a flue gas stream having a temperature of at least about 80° C. (175° F.). In another embodiment, the flue gas stream has a temperature ranging from about 80° C. to about 150° C. (300° F.). While the temperature of the flue gas stream can always be higher, for practical reasons this is generally not the case unless the original combustion device (e.g., heater, boiler, etc.) was poorly designed and highly inefficient. In addition, the flue gas stream can have a lower temperature in the case where a configuration that includes pre-cooling of the flue gas or input from a cooled gas sources such as wet FGD effluent is used.

The incoming flue gas stream may further contain other gases such as, for example, O<sub>2</sub>, NO<sub>x</sub> and SO<sub>x</sub>. Therefore, the aqueous ionic absorbent solutions used in step (a) of the method according to the present invention may also co-absorb one or more of, for example, SO<sub>2</sub>, NO<sub>x</sub>, COS, and SO<sub>x</sub> present in the gas stream. Thus, the aqueous ionic solutions may be employed to capture all or some of the pollutants in addition to CO<sub>2</sub> which are present in the gas stream.

The aqueous ionic absorbent solution will include (a) a diluent; and (b) an ionic absorbent containing a cation and an anion comprising an amine moiety. A suitable diluent includes, by way of example, inert diluents such as water, monohydric alcohols, polyols, and the like and mixtures thereof. Representative examples of suitable monohydric alcohols include C<sub>1</sub> to C<sub>12</sub> alcohols such as methanol, ethanol, isopropanol, 1-propanol, 1-butanol, 2-butanol, t-butanol, 2-methyl-1-propanol, 1-pentanol, 1-hexanol, 1-heptanol, 4-heptanol, 1-octanol, 1-nonyl alcohol, 1-decanol, 1-dodecanol and the like and mixtures thereof.

The polyols for use as a diluent include those having from 2 to about 10 carbon atoms and from two to six hydroxyl groups. Representative examples of suitable polyols include glycerol, triethylene glycol, 2-ethylene glycol, diethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, tetraethylene glycol, hexylene glycol and the like and mixtures thereof. In one preferred embodiment, the diluent is water.

In general, the amount of diluent added to the ionic absorbent is an amount capable of forming an absorption solvent having an acceptable viscosity to facilitate mass transfer of CO<sub>2</sub> into and out of the aqueous ionic absorbent solution in a carbon capture process. The ionic absorbents for use in forming the aqueous ionic absorbent solution have a relatively high viscosity in the absence of diluent. As such, the rate of CO<sub>2</sub> absorption for the ionic absorbents in the absence of one or more diluents is low and takes a relatively long time to reach equilibrium. It is particularly advantageous to use as little as water as possible so that less heat is used in the regenerator (H) discussed below, as long as a suitable viscosity of the aqueous ionic absorbent solution is achieved. This will lower the energy requirement for the method thereby resulting in an improvement in the total energy demand required to separate carbon dioxide (CO<sub>2</sub>) from an aqueous ionic absorbent solution.

In one embodiment, a suitable viscosity for the aqueous ionic absorbent solution in a carbon capture process will ordinarily range from about 0.1 to about 100 centistoke (cSt).

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In one embodiment, a suitable viscosity for the aqueous ionic absorbent solution in a carbon capture process can range from about 0.5 to about 20 cSt.

In one embodiment, the diluent content in the aqueous ionic absorbent solution is from about 25 wt. % to about 60 wt. % diluent, based on the total weight of the aqueous ionic absorbent solution. In one embodiment, the diluent content in the aqueous ionic absorbent solution is from about 40 to about 60 wt. %, based on the total weight of the aqueous ionic absorbent solution.

The ionic absorbent is generally composed of a cation and an anion. In one embodiment, the ionic absorbent is a liquid ionic absorbent and includes a category of compounds which are made up entirely of ions and are liquid at or below process temperatures including room temperature. The ionic liquids may have low melting points, for example, from -100° C. to 200° C. They tend to be liquid over a very wide temperature range, with a liquid range of up to about 500° C. or higher. Ionic liquids are generally non-volatile, with effectively no vapor pressure. Many are air and water stable, and can be good solvents for a wide variety of inorganic, organic, and polymeric materials. In another embodiment, the ionic absorbent is a solid ionic absorbent and includes a category of compounds which are made up entirely of ions and are solid in an anhydrous state at room temperature.

The ionic absorbent for use in forming the aqueous ionic absorbent solution of the present invention includes a cation and an anion comprising an amine moiety. The properties of the ionic absorbent can be tailored by varying the cation and anion pairing. The amine moiety advantageously provides selectivity for the aqueous ionic solution to complex with CO<sub>2</sub>.

In order for the aqueous ionic absorbent solutions containing the ionic absorbent to have a high volumetric/absorption capacity (mol CO<sub>2</sub>/mL absorbent), it is desirable to have the molecular weight of the neat ionic absorbent as low as possible to achieve the maximum molar concentration of ionic absorbent in the solution per weight of ionic absorbent basis which in turn will reduce the cost of the absorbent solution and the equipment size for the CO<sub>2</sub> capturing process.

It is believed that the cation group of the ionic absorbent has little impact on the molar CO<sub>2</sub> absorption capacity. Accordingly, the molecular weight of the cation can be as low as possible thereby lowering the overall molecular weight of the ionic absorbent. In one embodiment, the molecular weight of the cation can range from about 18 to about 500 atomic mass unit (AMU) (g/mole). In another embodiment, the molecular weight of the cation can range from about 18 to about 400 atomic mass unit (AMU) (g/mole).

In one embodiment, a cation is a secondary, tertiary or quaternary phosphonium cation represented by the general formula:



wherein R is the same or different and is hydrogen, a substituted or unsubstituted alkyl group, a substituted or unsubstituted fluoroalkyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted heteroaryl group, a substituted or unsubstituted arylalkyl group, a substituted or unsubstituted heteroalkyl group, or  $-(\text{CH}_2)_n-\text{R}'$ , wherein R' represents independently for each occurrence a substituted or unsubstituted

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tuted cycloalkyl group, a substituted or unsubstituted aryl group, or a substituted or unsubstituted heteroaryl group; and n represents independently for each occurrence an integer in the range 1 to 10 inclusive.

In one embodiment, a cation is a secondary, tertiary or quaternary ammonium cation represented by the general formula:



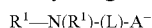
wherein R is the same or different and is hydrogen, a substituted or unsubstituted alkyl group, a substituted or unsubstituted fluoroalkyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted heteroaryl group, a substituted or unsubstituted arylalkyl group, a substituted or unsubstituted heteroalkyl group, or  $-(\text{CH}_2)_n-\text{R}'$ , wherein R' represents independently for each occurrence a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted aryl group, or a substituted or unsubstituted heteroaryl group, or three R groups together with the nitrogen atom to which they are bonded can be taken together to represent pyridinium, imidazolium, benzimidazolium, pyrazolium, benzpyrazolium, indazolium, thiazolium, benzthiazolium, oxazolium, benzoxazolium, isoxazolium, isothiazolium, imidazolidenium, guanidinium, quinuclidinium, triazolium, tetrazolium, quinolinium, isoquinolinium, piperidinium, pyrrolidinium, morpholinium, pyridazinium, pyrazinium, piperazinium, triazinium, azepinium, or diazepinium; and n represents independently for each occurrence an integer in the range 1 to 10 inclusive.

In another embodiment, the cation is a Group 1 or Group 2 metal of the Periodic Table. Representative examples of Group 1 metals include lithium, sodium, potassium, rubidium, cesium and the like. Representative examples of Group 2 metals include calcium, barium, magnesium, or strontium and the like.

In one embodiment, a cation includes, but is not limited to, a Group 1 or Group 2 metal of the Periodic Table, an ammonium cation, phosphonium cation, an imidazolium cation, a pyridinium cation, a pyrazolium cation, an oxazolium cation, a pyrrolidinium cation, a piperidinium cation, an alkyl thiazolium cation, an alkyl guanidinium cation, a morpholinium cation, a trialkylsulfonium cation, a triazolium cation, and the like.

In one, embodiment, a cation is a trialkyl or a tetraalkyl ammonium cation or phosphonium cation in which the alkyl group of the trialkyl or tetraalkyl is the same or different and is a  $\text{C}_1$  to  $\text{C}_{30}$  straight or branched, substituted or unsubstituted alkyl group. In another embodiment, a cation is a tetraalkyl ammonium cation or a tetraalkyl phosphonium cation in which the alkyl group of the tetraalkyl is the same or different and is a  $\text{C}_1$  to  $\text{C}_6$  straight or branched, substituted or unsubstituted alkyl group. The cation may contain ring structures where the N or P atom is a part of the ring structure.

Suitable anions for the ionic absorbent include those represented by the general formula:



wherein  $\text{R}^1$  is the same or different and includes hydrogen, a straight or branched  $\text{C}_1$  to  $\text{C}_{30}$  substituted or unsubstituted alkyl group, a  $\text{C}_1$  to  $\text{C}_{20}$  ester-containing group, a substituted or unsubstituted  $\text{C}_3$  to  $\text{C}_{30}$  cycloalkyl group, a substituted or unsubstituted  $\text{C}_3$  to  $\text{C}_{30}$  cycloalkylalkyl group, a substituted

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or unsubstituted  $\text{C}_3$  to  $\text{C}_{30}$  cycloalkenyl group, a substituted or unsubstituted  $\text{C}_5$  to  $\text{C}_{30}$  aryl group, a substituted or unsubstituted  $\text{C}_5$  to  $\text{C}_{30}$  arylalkyl group, a substituted or unsubstituted  $\text{C}_5$  to  $\text{C}_{30}$  heteroaryl group, a substituted or unsubstituted  $\text{C}_3$  to  $\text{C}_{30}$  heterocyclic ring, a substituted or unsubstituted  $\text{C}_4$  to  $\text{C}_{30}$  heterocyclolalkyl group, a substituted or unsubstituted  $\text{C}_6$  to  $\text{C}_{30}$  heteroarylalkyl group, or R and  $\text{R}^1$  together with the nitrogen atom to which they are bonded are joined together to form a heterocyclic group; L is a linking group, which can be a bond, or a divalent group selected from the group consisting of a straight or branched  $\text{C}_1$  to  $\text{C}_{30}$  substituted or unsubstituted alkyl group, a  $\text{C}_1$  to  $\text{C}_{20}$  ester-containing group, a substituted or unsubstituted  $\text{C}_3$  to  $\text{C}_{30}$  cycloalkyl group, a substituted or unsubstituted  $\text{C}_3$  to  $\text{C}_{30}$  cycloalkylalkyl group, a substituted or unsubstituted  $\text{C}_3$  to  $\text{C}_{30}$  cycloalkenyl group, a substituted or unsubstituted  $\text{C}_5$  to  $\text{C}_{30}$  aryl group, a substituted or unsubstituted  $\text{C}_5$  to  $\text{C}_{30}$  arylalkyl group, a substituted or unsubstituted  $\text{C}_5$  to  $\text{C}_{30}$  heteroaryl group, a substituted or unsubstituted  $\text{C}_3$  to  $\text{C}_{30}$  heterocyclic ring, a substituted or unsubstituted  $\text{C}_4$  to  $\text{C}_{30}$  heterocyclolalkyl group, a substituted or unsubstituted  $\text{C}_6$  to  $\text{C}_{30}$  heteroarylalkyl group and the like; and  $\text{A}^-$  is an anionic moiety.

In one embodiment,  $\text{A}^-$  is  $\text{SO}_3^-$  or  $\text{PO}_4^-$  or a conjugate base of multivalent acid.

In one embodiment, R and  $\text{R}^1$  are hydrogen or a straight or branched  $\text{C}_1$  to  $\text{C}_6$  substituted or unsubstituted alkyl group, L is a divalent straight or branched  $\text{C}_1$  to  $\text{C}_6$  substituted or unsubstituted alkyl group and  $\text{A}^-$  is  $\text{SO}_3^-$ .

Representative examples of alkyl groups for use herein include, by way of example, a straight or branched alkyl chain containing carbon and hydrogen atoms of from 1 to about 30 carbon atoms and preferably from 1 to about 6 carbon atoms with or without unsaturation, to the rest of the molecule, e.g., methyl, ethyl, n-propyl, 1-methylethyl (isopropyl), n-butyl, n-pentyl, etc., and the like.

Representative examples of fluoroalkyl groups for use herein include, by way of example, a straight or branched alkyl group as defined herein having one or more fluorine atoms attached to the carbon atom, e.g.,  $-\text{CF}_3$ ,  $-\text{CF}_2\text{CF}_3$ ,  $-\text{CH}_2\text{CF}_3$ ,  $-\text{CH}_2\text{CF}_2\text{H}$ ,  $-\text{CF}_2\text{H}$  and the like.

Representative examples of substituted or unsubstituted cycloalkyl groups for use herein include, by way of example, a substituted or unsubstituted non-aromatic mono or multi-cyclic ring system of about 3 to about 20 carbon atoms such as, for example, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, bridged cyclic groups or spirobicyclic groups, e.g., spiro-(4,4)-non-2-yl and the like, optionally containing one or more heteroatoms, e.g., O and N, and the like.

Representative examples of substituted or unsubstituted cycloalkylalkyl groups for use herein include, by way of example, a substituted or unsubstituted cyclic ring-containing group containing from about 3 to about 20 carbon atoms directly attached to the alkyl group which are then attached to the main structure of the monomer at any carbon from the alkyl group that results in the creation of a stable structure such as, for example, cyclopropylmethyl, cyclobutylethyl, cyclopentylethyl and the like, wherein the cyclic ring can optionally contain one or more heteroatoms, e.g., O and N, and the like.

Representative examples of substituted or unsubstituted cycloalkenyl groups for use herein include, by way of example, a substituted or unsubstituted cyclic ring-containing group containing from about 3 to about 20 carbon atoms with at least one carbon-carbon double bond such as, for example, cyclopropenyl, cyclobutenyl, cyclopentenyl and the like, wherein the cyclic ring can optionally contain one or more heteroatoms, e.g., O and N, and the like.

Representative examples of substituted or unsubstituted aryl groups for use herein include, by way of example, a substituted or unsubstituted monoaromatic or polyaromatic group containing from about 5 to about 20 carbon atoms such as, for example, phenyl, naphthyl, tetrahydronaphthyl, indenyl, biphenyl and the like, optionally containing one or more heteroatoms, e.g., O and N, and the like.

Representative examples of substituted or unsubstituted arylalkyl groups for use herein include, by way of example, a substituted or unsubstituted aryl group as defined herein directly bonded to an alkyl group as defined herein, e.g.,  $-\text{CH}_2\text{C}_6\text{H}_5$ ,  $-\text{C}_2\text{H}_5\text{C}_6\text{H}_5$  and the like, wherein the aryl group can optionally contain one or more heteroatoms, e.g., O and N, and the like.

Representative examples of fluoroaryl groups for use herein include, by way of example, an aryl group as defined herein having one or more fluorine atoms attached to the aryl group.

Representative examples of ester groups for use herein include, by way of example, a carboxylic acid ester having one to 20 carbon atoms and the like.

Representative examples of heterocyclic ring groups for use herein include, by way of example, a substituted or unsubstituted stable 3 to about 30 membered ring group, containing carbon atoms and from one to five heteroatoms, e.g., nitrogen, phosphorus, oxygen, sulfur and mixtures thereof. Suitable heterocyclic ring groups for use herein may be a monocyclic, bicyclic or tricyclic ring system, which may include fused, bridged or spiro ring systems, and the nitrogen, phosphorus, carbon, oxygen or sulfur atoms in the heterocyclic ring group may be optionally oxidized to various oxidation states. In addition, the nitrogen atom may be optionally quaternized; and the ring radical may be partially or fully saturated (i.e., heteroaromatic or heteroaryl aromatic). Examples of such heterocyclic ring functional groups include, but are not limited to, azetidiny, acridinyl, benzodioxolyl, benzodioxanyl, benzofuranyl, carbazolyl, cinnolinyl, dioxolanyl, indoliziny, naphthyridinyl, perhydroazepinyl, phenazinyl, phenothiazinyl, phenoxazinyl, phthalazinyl, pyridyl, pteridinyl, purinyl, quinoxalinyl, quinolinyl, isoquinolinyl, tetrazolyl, imidazolyl, tetrahydroquinolinyl, tetrahydroisoquinolinyl, piperidinyl, piperazinyl, 2-oxopiperazinyl, 2-oxopiperidinyl, 2-oxopyrrolidinyl, 2-oxoazepinyl, azepinyl, pyrrolyl, 4-piperidinyl, pyrrolidinyl, pyrazinyl, pyrimidinyl, pyridazinyl, oxazolyl, oxazoliny, oxazolidinyl, triazolyl, indanyl, isoxazolyl, iso-oxazolidinyl, morpholinyl, thiazolyl, thiazolinyl, thiazolidinyl, isothiazolyl, quinuclidinyl, isothiazolidinyl, indolyl, isoindolyl, indolinyl, isoindolinyl, octahydroindolyl, octahydroisoindolyl, quinolyl, isoquinolyl, decahydroisoquinolyl, benzimidazolyl, thiadiazolyl, benzopyranyl, benzothiazolyl, benzoaxazolyl, furyl, tetrahydrofuryl, tetrahydropyranyl, thienyl, benzothieryl, thiamorpholinyl, thiamorpholinyl sulfoxide, thiamorpholinyl sulfone, dioxaphospholanyl, oxadiazolyl, chromanyl, isochromanyl and the like and mixtures thereof.

Representative examples of heterocycloalkyl groups for use herein include, by way of example, a substituted or unsubstituted heterocyclic ring group as defined herein directly bonded to an alkyl group as defined herein. The heterocycloalkyl moiety may be attached to the main structure at carbon atom in the alkyl group that results in the creation of a stable structure.

Representative examples of heteroaryl groups for use herein include, by way of example, a substituted or unsubstituted heterocyclic ring group as defined herein. The het-

eroaryl ring radical may be attached to the main structure at any heteroatom or carbon atom that results in the creation of a stable structure.

Representative examples of heteroarylalkyl groups for use herein include, by way of example, a substituted or unsubstituted heteroaryl ring group as defined herein directly bonded to an alkyl group as defined herein. The heteroarylalkyl moiety may be attached to the main structure at any carbon atom from the alkyl group that results in the creation of a stable structure.

It will be understood that the term "substituted with" includes the implicit proviso that such substitution is in accordance with permitted valence of the substituted atom and the substituent, and that the substitution results in a stable compound, e.g., which does not spontaneously undergo transformation such as by rearrangement, cyclization, elimination, or other reaction. Representative examples of such substituents include, but are not limited to, hydrogen, fluorine, hydroxyl groups, halogen group, carboxyl groups, cyano groups, nitro groups, oxo ( $=\text{O}$ ), thio ( $=\text{S}$ ), substituted or unsubstituted alkyl, substituted or unsubstituted fluoroalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted aryl, substituted or unsubstituted arylalkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted cycloalkenyl, substituted or unsubstituted amino, substituted or unsubstituted aryl, substituted or unsubstituted heteroaryl, substituted heterocycloalkyl ring, substituted or unsubstituted heteroarylalkyl, substituted or unsubstituted heterocyclic ring, and the like.

Representative examples of ionic absorbents for use in the aqueous ionic absorbent solutions of the present invention includes tetrabutylammonium N-propyl-N-(3-sulfopropyl) amine, tetrabutylphosphonium N-isopropyl-N-(3-sulfopropyl)amine, tetraethylammonium N-isopropyl-N-(3-sulfopropyl)amine (TEA), tetramethylammonium N-isopropyl-N-(3-sulfopropyl)amine (TMA), tetramethyl ammonium N-propyl-N-(3-sulfopropyl)amine and the like and mixtures thereof.

The ionic absorbents for use in the process of the present invention are known and can be prepared by methods known in the art, e.g., as disclosed in U.S. Pat. Nos. 7,208,605 and 7,744,838 and WO 2008/122030, the contents of which are incorporated by reference herein. For example, in one embodiment, the ionic absorbents can be prepared in accordance with the synthetic schemes generally represented in FIGS. 1 and 2 (reactions with primary amines, secondary amines or diamines) via a zwitterionic intermediate. In one embodiment, the ionic absorbents can be prepared in accordance with the synthetic scheme generally represented in FIG. 3 in which the zwitterionic intermediate can be reacted with an epoxide. In one embodiment, the ionic absorbents can be prepared in accordance with the synthetic scheme generally represented in FIG. 4.

While the above examples have shown the reaction of the zwitterionic intermediates with ammonium hydroxide salts, as the base, one may also use other cations as described above, e.g., a phosphonium cation, a heterocyclic (e.g., imidazolium or pyridinium) cation, alkali metal cation or an alkaline earth metal cation as the counterion. In certain embodiments, the cations can be metal cations, such as Na, K, Ca, Ba, etc.

While the selected synthetic routes described above have all suggested reacting hydroxide salts of various cations with the zwitterions, other synthetic approaches can be envisioned as well, such as zwitterion deprotonation with strong bases like NaH or BuLi, followed by an ion metathesis step to exchange the Na or Li for a different cation.



As one skilled in the art will readily appreciate, in the case where the flue gas contains sufficient water vapor, the ionic absorbent can be used as is, i.e., neat. In other words, when there is a sufficient amount of water vapor in the flue gas, the sufficient amount of water and ionic absorbent will form an aqueous ionic absorbent solution having a viscosity suitable for use in the process of the present invention. A suitable viscosity for the aqueous ionic absorbent solution containing the ionic absorbent in the process of the present invention will ordinarily be from about 0.1 to about 100 centistoke (cSt). In one embodiment, a suitable viscosity for the aqueous ionic absorbent solution containing the ionic absorbent in the process of the present invention can range from about 0.5 to about 40 cSt.

As discussed above, in order for the aqueous ionic absorbent solutions to have a sufficiently high volumetric adsorption capacity for CO<sub>2</sub> (mol CO<sub>2</sub>/cm<sup>3</sup> solvent), the molecular weight of the neat ionic absorbent should be as low as possible, e.g., a molecular weight of no more than about 700 atomic mass unit (AMU) (g/mole). In one embodiment, the molecular weight of the neat ionic absorbent is from about 75 to about 700 AMU (g/mole). In one embodiment, the molecular weight of the neat ionic absorbent is below about 600 AMU (g/mole). In another embodiment, the molecular weight of the neat ionic absorbent is from about 75 to about 600 AMU (g/mole). In one embodiment, the molecular weight of the neat ionic absorbent is below about 500 AMU (g/mole). In another embodiment, the molecular weight of the neat ionic absorbent is from about 75 to about 500 AMU (g/mole).

In general, the flue gas stream containing CO<sub>2</sub> is contacted with an aqueous ionic absorbent solution under absorption conditions to absorb at least a portion of the CO<sub>2</sub> from the flue gas stream and form a CO<sub>2</sub>-aqueous ionic absorbent solution stream. The absorption conditions for contacting the flue gas stream with the aqueous ionic absorbent solution include conducting the absorption process at around ambient pressure (i.e. approximately 1 bar) or a pressure slightly higher than ambient pressure, i.e., a pressure of from 1.1 to about 1.5 bar, the flue gas stream has a temperature of about 80° C. to about 120° C. and the aqueous ionic absorbent solution has a temperature of about 20° C. to about 60° C.

Once the CO<sub>2</sub> is substantially removed from the flue gas stream, the CO<sub>2</sub>-aqueous ionic absorbent solution stream is then subjected to desorption conditions to form a CO<sub>2</sub>-rich stream and an aqueous ionic absorbent solution stream having a reduced CO<sub>2</sub> content. It is also advantageous to use an aqueous ionic absorbent solution having a relatively low heat of absorption in the desorption step (b). We found that the ionic absorbent used in the method of the present invention has a significantly lower heat of absorption than the reference monoethanolamine (MEA). For example, tetraethylammonium N-isopropyl-N-(3-sulfopropyl)amine with 50 wt. % water gave a heat of absorption of -54 kJ/mol with X<sub>CO2</sub>=0.76 and tetraethylammonium N-butyl-N-(3-sulfopropyl)amine with 50 wt. % water gave heat of absorption of -32 kJ/mol at X<sub>CO2</sub>=0.48. The reaction of CO<sub>2</sub> absorption by the aqueous ionic absorbent solution is an exothermic reaction. Therefore, the reported values are the magnitude of the heat of absorption in units of kJ per mol of CO<sub>2</sub>. For a comparative example, 30 wt. % monoethanolamine in 70 wt. % water, the heat of absorption is known to be approximately -80 kJ per mol of CO<sub>2</sub> at 40° C.

It is believed that by employing an aqueous ionic absorbent solution having a heat of absorption lower than the heat of absorption for 30 wt. % monoethanolamine in 70 wt. % water, the energy required to reverse the absorption reaction and

release CO<sub>2</sub> in the solvent regeneration column is decreased by about 30 to about 60%. Therefore, one could utilize the low heat of absorption for CO<sub>2</sub> by the aqueous ionic absorbent solution of the present invention to reduce the total energy demand required for post-combustion carbon capture process to separate carbon dioxide (CO<sub>2</sub>) from the CO<sub>2</sub>-rich aqueous ionic absorbent solution stream.

Generally, solvent regeneration is the most energy intensive step in a post-combustion CO<sub>2</sub> capture process, where CO<sub>2</sub> is desorbed from the CO<sub>2</sub>-rich aqueous ionic absorbent solution stream, and then the desorbed CO<sub>2</sub> is captured and CO<sub>2</sub>-lean absorbent solution is returned to the absorber for another cycle. The energy required for solvent regeneration has three components. Energy added to the solvent regenerator is used to (1) heat the solvent to the regeneration temperature, which is commonly referred to as sensible heat; (2) produce steam, which acts as a stripping agent, and (3) provide energy to reverse the absorption reaction. The energy required to reverse the absorption reaction is a major component of the total energy required for solvent regeneration. With the lower heat of absorption, the ionic absorbent of the aqueous ionic absorbent solution used in the method of the present invention would require much lower energy to desorb the CO<sub>2</sub> from the CO<sub>2</sub>-rich aqueous ionic absorbent solution stream.

In addition, for the aqueous ionic absorbent solution stream used in the method of the present invention, the sensible heat demand could also be lowered by decreasing the water or diluent content of the aqueous ionic absorbent solution stream as discussed above. Due to the lower heat of absorption estimated for the aqueous ionic absorbent solution used in the method of the present invention, and by selecting optimal process conditions for the ionic absorbent of this invention, these solutions are believed to provide for a lower overall energy requirement for solvent regeneration, which will provide a more energy efficient process for CO<sub>2</sub> removal from a gas stream such as a flue gas stream. While it is difficult to estimate the exact savings in total energy for the post-combustion CO<sub>2</sub> capturing process, it is believed that at least 10% of energy savings could be achieved by the method of the present invention compared with 30 wt. % monoethanolamine in 70 wt. % water:

In one embodiment, the aqueous ionic absorbent solution will have a heat of absorption of about 20 to no more than about 70 kJ/mol of CO<sub>2</sub> at a temperature ranging from about 20° C. to about 95° C. In another embodiment, the aqueous ionic absorbent solution will have a heat of absorption of about 25 to no more than about 60 kJ/mol of CO<sub>2</sub> at a temperature ranging from about 20° C. to about 95° C.

The heat of absorption of the aqueous ionic absorbent solution can be determined by methods known in the art. In general, the energy requirement for solvent regeneration is an important consideration in selecting a CO<sub>2</sub>-removal solvent. One commonly-used parameter to assess the regeneration energy requirements is the isosteric heat of sorption, which can be estimated by the formula:

$$\Delta H_{CO_2} = R \left( \frac{\partial \ln(P_{CO_2})}{\partial (1/T)} \right)_{X_{CO_2}}$$

wherein  $\Delta H_{CO_2}$  is the heat of absorption (kJ/mol) at a given CO<sub>2</sub> liquid loading, X<sub>CO2</sub> (mol CO<sub>2</sub>/mol of ionic absorbent), P<sub>CO2</sub> (psia) and T (K) are the absolute partial pressure of CO<sub>2</sub> and absolute temperature, respectively, and R is the gas constant, 8.314 J/mol\*K.  $\Delta H_{CO_2}$  will have a negative value in

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most cases (indicating that the absorption of  $\text{CO}_2$  by the solvent is an exothermic reaction).  $\Delta H_{\text{CO}_2}$  can be calculated by measuring the loading curves for  $\text{CO}_2$  at two or more temperatures and plotting the data for a fixed value of  $X_{\text{CO}_2}$  as  $\ln(P_{\text{CO}_2})$  vs  $1/T$ . The slope of the resulting plot multiplied by  $R$  is the heat of absorption.

In general, desorption condition include carrying out the desorption process in which the pressure of the  $\text{CO}_2$ -aqueous ionic absorbent solution stream is greater than about 1.9 bar to about 10 bar. In one embodiment, the pressure of the  $\text{CO}_2$ -aqueous ionic absorbent solution stream is about 4 bar to about 8 bar. The pressurized  $\text{CO}_2$ -aqueous ionic absorbent solution stream is also heated to a temperature of about  $90^\circ\text{C}$ . to about  $200^\circ\text{C}$ .

In one embodiment, when the flue gas stream is first pre-cooled to a temperature of about  $40^\circ\text{C}$ . to about  $60^\circ\text{C}$ . and then sent to the absorber and contacted with ionic absorbent stream, the desorption conditions for removing carbon dioxide from the  $\text{CO}_2$ -rich aqueous ionic absorbent solution stream may include heating the  $\text{CO}_2$ -rich aqueous ionic absorbent solution stream to a temperature of greater than  $60^\circ\text{C}$ . to about  $80^\circ\text{C}$ . in the case where the regenerator (i.e., stripper) is run at vacuum conditions.

In another embodiment, when the flue gas stream is first pre-cooled to a temperature of about  $40^\circ\text{C}$ . to about  $60^\circ\text{C}$ . and then sent to the absorber and contacted with the ionic absorbent stream, the desorption conditions for removing carbon dioxide from  $\text{CO}_2$ -rich aqueous ionic absorbent solution stream may include heating the  $\text{CO}_2$ -rich aqueous ionic absorbent solution stream to a temperature of greater than  $100^\circ\text{C}$ . to about  $120^\circ\text{C}$ . in the case where the regenerator is run at atmospheric conditions.

In one embodiment, when the flue gas stream is sent to the absorber at a temperature of about  $60^\circ\text{C}$ . to about  $80^\circ\text{C}$ ., the desorption conditions for removing carbon dioxide from the  $\text{CO}_2$ -rich aqueous ionic absorbent solution stream may include heating the  $\text{CO}_2$ -rich aqueous ionic absorbent solution stream to a temperature of about  $100^\circ\text{C}$ . to about  $200^\circ\text{C}$ . in the case where the regenerator is run at atmospheric or high-pressure conditions.

In one embodiment, when the flue gas stream is sent to the absorber at a temperature of about  $80^\circ\text{C}$ . to about  $100^\circ\text{C}$ ., the desorption conditions for removing carbon dioxide from the  $\text{CO}_2$ -rich aqueous ionic absorbent solution stream may include heating the  $\text{CO}_2$ -rich aqueous ionic absorbent solution stream to a temperature of about  $120^\circ\text{C}$ . to about  $200^\circ\text{C}$ . in the case where the regenerator is run at atmospheric or high-pressure conditions.

In one embodiment, the method of the present invention will be explained in more detail on the basis of the accompanying figure and the following examples.

FIG. 5 is a diagrammatic view of a plant suitable for carrying out the method according to the present invention. In general, FIG. 5 includes a carbon dioxide ( $\text{CO}_2$ ) separation system for recovering high purity  $\text{CO}_2$  from flue gas stream (A). First, flue gas stream (A) enters blower (W1), which blows flue gas stream (B) to absorber (D). Blower (W1) can be any type of blower known to one skilled in the art. Generally, the pressure of flue gas stream (A) is around 1 bar. Blower (B) raises the pressure of the flue gas stream to a pressure ranging from 1.1 to about 1.5 bar. The pressure is typically raised to overcome the pressure drop associated with flowing the gas through the absorber tower.

In one embodiment, absorber (D) is a packed tower. The packing may be random packing, structured packing or any combination thereof. The randomly packed material can include, but is not limited to, Raschig rings, saddle rings, Pall

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rings, or any other known type of packing ring, or combination of packing rings. The structured packed material can include, but is not limited to, corrugated sheets, crimped sheets, gauzes, grids, wire mesh, monolith honeycomb structures, or any combination thereof. Examples of structured packing include Sulzer DX™, Mellapak™, Mellapak Plus™, Katapak™, and the like.

As discussed above, water present in the flue gas stream will form an aqueous solution containing the ionic absorbent. If the viscosity of the aqueous solution is not sufficient for use in the process of the present invention, then it may be necessary to add one or more diluents to the aqueous solution to further reduce its viscosity to a viscosity suitable for the process of the present invention. Accordingly, a diluent stream (G) is present at the top of the column to further hydrate the incoming ionic liquid stream (C) and reduce its viscosity as discussed above. In addition, diluent stream (G) can scrub any additional diluent that may be carried over into treated flue gas stream (A1) leaving the absorber (D) to partly or completely remove any unwanted impurities. Typically, the total amount of water and diluents, when present, in the aqueous ionic absorbent solution is largely dictated by viscosity requirements, and is generally less than about 80 wt. %. In one embodiment, the total amount of water present in the aqueous ionic absorbent solution is from about 15 wt. % to about 80 wt. %. In one embodiment, the total amount of water present in the aqueous ionic absorbent solution is from about 30 wt. % to about 60 wt. %.

The flue gas stream (A) and ionic absorbent stream (C) are contacted in absorber (D). In general, flue gas stream (A) is introduced into chemical absorber (D) and during the process of flow from the bottom up, the carbon dioxide in flue gas stream (A) is absorbed by ionic absorbent (C) flowing from the top down. The end gas, i.e., treated flue gas stream (A1), which is essentially depleted of carbon dioxide, is introduced out of the absorber, for example, through a vent from the top of the absorber after contacting (or being scrubbed) by diluent stream G. In one embodiment, from about 80 to about 95% of  $\text{CO}_2$  in stream A has been removed to form stream A1.

The ionic absorbent stream (E), which has absorbed carbon dioxide ( $\text{CO}_2$ -rich aqueous ionic absorbent solution stream), comes out of absorber (D) from the bottom and is pumped to cross exchanger (K), where its temperature is raised; and then the preheated stream (F) may be pumped through pump (W2). Pump (W2) raises the pressure of ionic absorbent stream (E) to greater than about 1.9 bar to provide pressurized ionic absorbent stream (F1). In one embodiment, the pressure of ionic absorbent stream (E) is raised to a pressure of greater than about 1.9 bar to about 10 bar. In one embodiment, the pressure is raised to about 4 bar to about 8 bar. Pump (W2) can be any apparatus capable of raising the pressure of preheated stream (F) such as, for example, a centrifugal pump, a reciprocating pump, a gear pump, etc.

Next, pressurized ionic absorbent stream (F1) is sent to the top of regenerator (H) (i.e., stripper) to flow down through the regenerator where it is further heated to a temperature ranging from about  $90^\circ\text{C}$ . to about  $200^\circ\text{C}$ . by, for example, steam-heated or hot-oil heated reboiler and under vacuum, atmospheric or high pressure conditions. In one embodiment, pressurized ionic absorbent stream (F1) is sent to the top of regenerator (H) to flow down through the regenerator where it is further heated to a temperature of about  $120^\circ\text{C}$ . to about  $180^\circ\text{C}$ . In this manner, most of the carbon dioxide in the ionic liquid (F1) is released as a wet carbon dioxide gas stream (L) and emitted out from the top of regenerator (H). Regenerator (H) is a packed tower and can be any random or structure packing as discussed above with absorber (D). The high tem-

perature regeneration allows for greater flexibility in using different levels of steam and/or waste heat resources in reboiler (Q), as discussed below. The regenerator (H) is typically run at relatively high pressure, e.g., a pressure from about 1.9 bar to about 10 bar. By running regenerator (H) at a relatively high pressure, carbon dioxide stream (L) may be recovered at higher pressure thereby reducing the capital and operating costs associated with carbon dioxide compression (Y), discussed below. The ionic absorbent depleted of carbon dioxide, i.e., ionic absorbent stream (S), is emitted out from the bottom of regenerator (H).

In one embodiment, when flue gas stream (A) is first pre-cooled to a temperature of about 40° C. to about 60° C. and then sent to the absorber and contacted with ionic absorbent stream (C), the desorption conditions for removing carbon dioxide from ionic absorbent stream (F1) may include heating stream (F1) to a temperature of greater than 60° C. to about 80° C. in the case where the regenerator (i.e., stripper) is run at vacuum conditions. In another embodiment, when flue gas stream (A) is first pre-cooled to a temperature of about 40° C. to about 60° C. and then sent to the absorber and contacted with ionic absorbent stream (C), the desorption conditions for removing carbon dioxide from pressurized ionic absorbent stream (F1) may include heating stream (F1) to a temperature of greater than 100° C. to about 120° C. in the case where the regenerator is run at atmospheric conditions. In yet another embodiment, when flue gas stream (A) is first pre-cooled to a temperature of about 40° C. to about 60° C. and then sent to the absorber and contacted with ionic absorbent stream (C), the desorption conditions for removing carbon dioxide from pressurized ionic absorbent stream (F1) may include heating stream (F1) to a temperature of about 120° C. to about 200° C. in the case where the regenerator is run at high-pressure conditions (i.e., 1.9 to 10 bar).

In one embodiment, when flue gas stream (A) is sent to the absorber at a temperature of about 60° C. to about 80° C., the desorption conditions for removing carbon dioxide from pressurized ionic absorbent stream (F1) may include heating stream (F1) to a temperature of about 100° C. to about 200° C. in the case where the regenerator is run at atmospheric or high-pressure conditions.

In one embodiment, when flue gas stream (A) is sent to the absorber at a temperature of about 80° C. to about 100° C., the desorption conditions for removing carbon dioxide from pressurized ionic absorbent stream (F1) may include heating stream (F1) to a temperature of about 120° C. to about 200° C. in the case where the regenerator is run at atmospheric or high-pressure conditions.

The wet carbon dioxide gas stream (L) coming from the top of regenerator (H) is then passed through cooler (M), such as a condenser, where it is cooled to provide cooled carbon dioxide gas stream (N). The temperature of carbon dioxide gas stream (L) is generally decreased to about 30° C. to about 50° C. The cooled carbon dioxide gas stream (N) is sent to separator (O) where condensed water and trace amounts of ionic absorbent and optional diluents (P1) and (P2) are separated and (P1) is returned to regenerator (H) as reflux (P1). The gas stream (R), as the carbon dioxide product, is sent to gas injection regulatory system (X) where it is dehydrated using methods known in the art, e.g., triethylene glycol dehydration or heatless absorption using molecular sieves. The dehydrated gas is then sent to compressor (Y) to be pressurized, under normal pressure and a temperature of less than about 60° C., to about 7.4 MPa or higher, and sent off to pipeline (Z). In one embodiment, the captured CO<sub>2</sub> can be used on-site or can be made available for sale to a co-located facility. Dried CO<sub>2</sub> will be compressed in a series of compres-

sors and intercoolers to a final temperature of about 40° C. to about 60° C. The last compression stage would be close to the supercritical pressure of CO<sub>2</sub> (i.e., about 1100 psig). Once CO<sub>2</sub> is supercritical, it may be pumped as a dense phase fluid to any pressure required for transportation—final dense phase pressure may range from about 100 to about 200 bar.

The reboiler (O) is a shell and tube heat exchanger. Ionic absorbent stream (S) coming from the bottom of the regenerator (H) enters into the tubes of the reboiler (O) where it is heated by steam in the shell-side of the reboiler. Stream (T) is the supply heating medium, such as steam that it is available from the facility generating the flue gas (e.g., refinery, gas/oil-fired boiler, power plant, etc.) while stream (U) is the return condensate that is returned back to the utility system of the facility. Therefore, the ionic absorbent stream (S) is heated in the reboiler (O) and at least a portion of the carbon dioxide and water vapor present therein is released out and leaves from the top of reboiler (O) into regenerator (H) as stripping gas (I). On the other hand, ionic absorbent solution (J) with significantly decreased content of absorbed carbon dioxide (also referred to as “CO<sub>2</sub>-lean absorbent solution”) is sent back to cross exchanger (K).

The following non-limiting examples are illustrative of the present invention.

Experiments were conducted to measure the CO<sub>2</sub> absorption of ionic absorbent materials diluted with water and to demonstrate their effectiveness.

The equilibrium CO<sub>2</sub> carrying capacity of the aqueous ionic absorbent solutions was measured via a volumetric method. A known quantity of ionic absorbent-water mixture is injected into a sealed pressure vessel containing high purity CO<sub>2</sub> gas at pressure of approximately 15 psia, and the vessel is shaken to provide mixing of the solution. The pressure in the vessel decreases as CO<sub>2</sub> is absorbed into the solution, and the pressure is monitored until the system reaches an equilibrium pressure. The temperature of the system is controlled and monitored, and an equilibrium pressure is measured for multiple temperatures in each experiment. The initial and final pressure of CO<sub>2</sub>, the volume of the pressure vessel, and the quantity and composition of the injected ionic absorbent-water mixture are all known.

The measured experimental data are used to calculate the loading of CO<sub>2</sub> in the solution, which is reported as moles of CO<sub>2</sub> bound per mol of ionic absorbent in the solution. An aqueous ionic absorbent solution is contacted in a sealed vessel with a low partial pressure CO<sub>2</sub> gas simulating a flue gas stream. The vessel is maintained at a constant temperature by way of heating tape and is shaken to allow good contact between CO<sub>2</sub> and the absorbent solution until the system reaches equilibrium. When the pressure reaches the steady state, then a pressure is recorded and the vessel temperature is changed to the next set point. Based on the equilibrium CO<sub>2</sub> pressure, the loading per mole of ionic absorbent is calculated. The measured pressure in the vessel is used to determine the moles of gaseous CO<sub>2</sub> present in the vessel before and after CO<sub>2</sub> absorption occurs (before and after the solvent is injected into the vessel) using the ideal gas equation of state:  $P_{CO_2} V = n R T$ , where  $P_{CO_2}$  = partial pressure of CO<sub>2</sub> (psia),  $V$  = volume of the gas phase in the vessel,  $n$  = total moles of CO<sub>2</sub> gas,  $T$  = measured experimental temperature in degrees Kelvin, and  $R$  is the Ideal Gas Constant, which has units of energy per mol per degree Kelvin (approximately 8.314 J/mol K).

The water vapor pressure in the vessel is determined assuming the solvent is an ideal mixture of water and absorbent using the known vapor pressure of water at the temperature of a given experiment (taken from the NIST steam tables,

see <http://webbook.nist.gov/chemistry/fluid>): the partial pressure of water in the vessel is calculated as the vapor pressure of water multiplied by the mol fraction of water in the solvent (which is known from the mass of water and absorbent used in preparing the solvent mixture). Because the ionic materials used as absorbents have negligibly low vapor pressure, the gas in the vessel is composed only of water and CO<sub>2</sub>. The partial pressure of CO<sub>2</sub> is calculated as the difference between the measured total pressure and the water vapor pressure. The difference between the gas-phase quantity of CO<sub>2</sub> before and after solvent injection is used to calculate the absorbed quantity of CO<sub>2</sub> for various temperatures in a single experiment. The absorbed quantity of CO<sub>2</sub> is then divided by the quantity of ionic material in the solvent to calculate the loading as moles of CO<sub>2</sub> absorbed per mole of ionic absorbent. For some experiments, the water vapor pressure over the aqueous ionic absorbent pressure was measured directly and used to more accurately determine the quantity of carbon dioxide absorbed.

## EXAMPLE 1

The effect of water addition to the ionic absorbents was studied using tetraethylammonium N-isopropyl-N-(3-sulfo-propyl)amine (TEA) as the ionic absorbent. Neat TEA is a very viscous material. The addition of water lowered the viscous nature of the TEA significantly. Varying amounts of water was added to the TEA and the time to reach the equilibrium CO<sub>2</sub> uptake was determined. The results are summarized below in Table 1.

TABLE 1

Water Diluent, Wt. %	Time to reach equilibrium CO <sub>2</sub> uptake	Viscosity (cSt) at 20° C.	Viscosity (cSt) at 80° C.
0	>>2 days	Very viscous	—
25	~24 hours	Viscous	—
50	<1 hour	10.5	1.7

As the data show, a neat ionic absorbent (i.e., TEA) provided a significantly longer time to approach equilibrium as compared to (1) the aqueous ionic absorbent solution containing TEA with 25 wt. % water and (2) the aqueous ionic absorbent solution containing TEA with 50 wt. % water, i.e., 2 days versus 24 hours and 1 hour, respectively. The lower viscosity of the aqueous ionic absorbent solution case facilitates rapid mass transfer of CO<sub>2</sub> between the gas and liquid phases, and enables CO<sub>2</sub> absorption to occur on a faster timescale as compared to the neat ionic absorbent which is mass-transfer limited due to the high viscosity of the absorbent. These results demonstrate that sufficient diluent content is necessary to achieve CO<sub>2</sub> removal from gas streams on an industrially-relevant timescale.

## EXAMPLE 2

Two 50 wt. % aqueous ionic absorbent solutions of ionic absorbent were prepared. The ionic absorbents were tetraethylammonium N-isopropyl-N-(3-sulfo-propyl)amine (TEA) and tetramethylammonium N-isopropyl-N-(3-sulfo-propyl)amine (TMA), respectively. The aqueous ionic absorbent solution was contacted in a sealed vessel with a low partial pressure CO<sub>2</sub> gas simulating a model flue gas stream. The vessel was maintained at a constant temperature and is shaken to allow good contact between CO<sub>2</sub> and the absorbent ionic absorbent solution until the system reached equilibrium. When the pressure reached the steady state, then a

pressure was recorded and then the vessel temperature was changed to the next set point. Based on the equilibrium CO<sub>2</sub> pressure, the loading per mole of ionic absorbent was calculated.

The CO<sub>2</sub> loading of the two ionic absorbents were plotted as a function of CO<sub>2</sub> partial pressure in FIG. 6. The data in this figure demonstrate that these solutions have high molar absorption capacities ranging from 0.5 to about 0.85 CO<sub>2</sub> absorption loading per mole of ionic absorbent. These absorption capacities are significantly higher than the conventional amine-based solvents such as monoethanolamine (MEA). The CO<sub>2</sub> loading for 30 wt. % MEA was also measured and the data are presented in FIG. 7 which shows 0.4 to 0.5 mol CO<sub>2</sub> absorbed per mole of MEA (comparative example).

## EXAMPLE 3

From the data in FIG. 6, the expected CO<sub>2</sub> removal capacity of the ionic absorbent from flue gas can be estimated. The plot shows that an aqueous ionic absorbent solution of TMA with 50 wt. % water can absorb up to 0.74 mol CO<sub>2</sub> per mol ionic absorbent at 40° C. with a CO<sub>2</sub> partial pressure of 2.8 psia. This condition is reflective of the “rich” solution loading in the absorber. The solution absorption capacity of the aqueous ionic absorbent solution for CO<sub>2</sub> at 95° C. and a CO<sub>2</sub> partial pressure of 5.0 psia decreases to 0.5 mol CO<sub>2</sub> per mol aqueous ionic solution. This second condition may reflect the “lean” solution loading achieved in the regeneration column. Therefore, the absorber-regenerator system described herein could remove 0.24 moles of CO<sub>2</sub> per mol of TMA ionic absorbent circulated through the absorber-regenerator system per pass.

Since the ionic absorbent for use in the aqueous ionic absorbent solution can be operated in a wide range of temperatures, the CO<sub>2</sub> capture process conditions can be chosen to increase the loading difference between the “rich” and “lean” CO<sub>2</sub> capacities. As one skilled in the art will readily appreciate, the chemical absorption capacity of solvent decreases with (1) decreasing partial pressure of the absorbed species in the gas phase and (2) increasing temperature. Therefore, by operating the stripper at temperatures in excess of 95° C., the CO<sub>2</sub> removal capacity of the system can be further increased. The removal capacity of the system can also be increased by operating the stripper with lower CO<sub>2</sub> partial pressure.

Therefore, the results show that that TMA would have the capacity to remove at least 0.24 moles of CO<sub>2</sub> per mol of ionic absorbent circulated through the absorber-regenerator system per pass.

## EXAMPLE 4

From the data in FIG. 6, the expected CO<sub>2</sub> removal capacity of TEA from flue gas can be estimated. The plot shows that an aqueous ionic absorbent solution of TEA with 50 wt. % water absorb up to 0.76 mol CO<sub>2</sub> per mol ionic absorbent at 40° C. with a CO<sub>2</sub> partial pressure of 1.2 psia. This condition is reflective of the “rich” solution loading in the absorber. In this TEA-based solution, the absorption capacity for CO<sub>2</sub> at 95° C. and a CO<sub>2</sub> partial pressure of 6.3 psia decreases to 0.57 mol CO<sub>2</sub> per mol aqueous ionic solution. This second condition may reflect the “lean” solution loading achieved in the regeneration column. Therefore, the absorber-regenerator system described herein could remove 0.19 moles of CO<sub>2</sub> per mol of aqueous ionic absorbent solution circulated through the absorber-regenerator system. As in the previous example,

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the CO<sub>2</sub> removal capacity of the system will be further increased by operating the stripper at higher temperatures and/or operating the stripper at lower CO<sub>2</sub> partial pressure.

Therefore, the results show that TEA would have the capacity to remove at least 0.19 moles of CO<sub>2</sub> per mol of ionic absorbent circulated through the absorber-regenerator system per pass.

#### COMPARATIVE EXAMPLE A

FIG. 7 shows measured CO<sub>2</sub> absorption data for an aqueous solution containing 30 wt. % MEA with 70 wt. % water. At 20° C., the absorption capacity for CO<sub>2</sub> at a CO<sub>2</sub> partial pressure of 1.5 psia was approximately 0.5 mol CO<sub>2</sub> per mol MEA, which reflects the loading in the absorption column. By heating the solution at 95° C. and a CO<sub>2</sub> partial pressure of 3.0 psia, the measured loading decreases to 0.4 mol CO<sub>2</sub> per mol of MEA. This second condition reflects the “lean” solution loading achieved in the regeneration column. Therefore, the absorber-regenerator system using an aqueous solution of MEA under these conditions could remove 0.10 moles of CO<sub>2</sub> per mol of MEA. When comparing Comparative Example A with Examples 2 and 3, the capacities of aqueous ionic absorbent solution containing TEA and TMA, respectively, for CO<sub>2</sub> are higher than that of aqueous MEA, measured as moles of CO<sub>2</sub> captured per mol of absorbent.

#### EXAMPLE 5

As described in Example 3, an aqueous ionic absorbent solution of TMA with 50 wt. % water can absorb up to 0.74 mol CO<sub>2</sub> per mol ionic absorbent at 40° C. with a CO<sub>2</sub> partial pressure of 2.8 psia. This condition is reflective of the “rich” solution loading in the absorber. The solution absorption capacity of the aqueous ionic absorbent solution for CO<sub>2</sub> at 120° C. and a CO<sub>2</sub> partial pressure of 5 psia was measured as 0.16 mol CO<sub>2</sub> per mol aqueous ionic absorbent solution. This second condition may reflect the “lean” solution loading achieved in the regeneration column. Therefore, the absorber-regenerator system described herein could remove 0.58 moles of CO<sub>2</sub> per mol of TMA ionic absorbent circulated through the absorber-regenerator system per pass.

Since the ionic absorbent for use in the aqueous ionic absorbent solution can be operated in a wide range of temperatures, the CO<sub>2</sub> capture process conditions can be chosen to increase the loading difference between the “rich” and “lean” CO<sub>2</sub> capacities. As one skilled in the art will readily appreciate, the chemical absorption capacity of solvent decreases with (1) decreasing partial pressure of the absorbed species in the gas phase and (2) increasing temperature. Therefore, by operating the stripper at temperatures in excess of 120° C., the CO<sub>2</sub> removal capacity of the system can be further increased. The removal capacity of the system can also be increased by operating the stripper with lower CO<sub>2</sub> partial pressure.

Therefore, the results show that that TMA would have the capacity to remove at least 0.58 moles of CO<sub>2</sub> per mol of ionic absorbent circulated through the absorber-regenerator system per pass.

#### COMPARATIVE EXAMPLE B

According to the equilibrium measurements of Shen and Li, J. Chem. Eng. Data, 37, pp. 96-100 (1992) at 40° C., the absorption capacity for CO<sub>2</sub> at a CO<sub>2</sub> partial pressure of 1 psia is approximately 0.5 mol CO<sub>2</sub> per mol MEA, which reflects the loading in the absorption column. The equilibrium CO<sub>2</sub>

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loading as measured by Ma'mun et. al., J. Chem. Eng. Data, 50, pp. 630-634 (2005) at 120° C. and a CO<sub>2</sub> partial pressure of 5.0 psia was 0.28 mol CO<sub>2</sub> per mol of MEA. This second condition reflects the “lean” solution loading achieved in the regeneration column. Therefore, the absorber-regenerator system using an aqueous solution of MEA under these conditions could remove 0.22 moles of CO<sub>2</sub> per mol of MEA. When comparing Comparative Example B with Example 5, the CO<sub>2</sub> removal capacity, measured as moles of CO<sub>2</sub> captured per mol of absorbent, of an aqueous ionic absorbent solution containing 50 wt. % TMA, is higher than that of an aqueous solution of 30 wt. % MEA.

#### EXAMPLE 6

Heat of absorption of TEA with 50 wt. % water was estimated based on FIG. 8, where 1/T in degree Kelvin is plotted against the natural log of P<sub>CO2</sub>, and an absolute partial pressure of CO<sub>2</sub> in psia for experimental measurements with a constant mol CO<sub>2</sub>/mol of absorbent of 0.76 (X<sub>CO2</sub>). From the slope of the plot, ΔH<sub>CO2</sub>, the heat of absorption (kJ/mol) at a given CO<sub>2</sub> liquid loading is calculated using the equation:

$$\Delta H_{CO_2} = R \left( \frac{\partial \ln(P_{CO_2})}{\partial (1/T)} \right)_{X_{CO_2}}$$

where ΔH<sub>CO2</sub> is the heat of absorption (kJ/mol) at a given CO<sub>2</sub> liquid loading, X<sub>CO2</sub> (mol CO<sub>2</sub>/mol of absorbent). P<sub>CO2</sub> (psia) and T(K) are the absolute partial pressure of CO<sub>2</sub> and absolute temperature, respectively, and R is the gas constant, 8.314 J/mol\*K. ΔH<sub>CO2</sub> will have a negative value in most cases (indicating that the absorption of CO<sub>2</sub> by the solvent is an exothermic reaction).

We measured -54 kJ/mol of CO<sub>2</sub> heat of absorption for TEA with 50 wt. % water at a fixed CO<sub>2</sub> loading of X<sub>CO2</sub>=0.76. This is about 30% lower than the comparative example of 30 wt % monoethanolamine in water with the heat of absorption of approximately -80 kJ per mol of CO<sub>2</sub> at 40° C. Because the significantly lower heat of absorption for the ionic absorbents disclosed herein, the energy required to reverse the absorption reaction and release CO<sub>2</sub> in the solvent regeneration column is expected to decrease significantly.

#### EXAMPLE 7

The heat of absorption of tetraethylammonium N-butyl-N-(3-sulfopropyl)amine (TEA-butyl) with 50 wt. % water was estimated based on FIG. 9, where 1/T in degree Kelvin is plotted against P<sub>CO2</sub>, and absolute partial pressure of CO<sub>2</sub> in psia for experimental measurements at a constant mol CO<sub>2</sub>/mol of absorbent of 0.48 (X<sub>CO2</sub>).

We measured -32 kJ/mol of CO<sub>2</sub> heat of absorption for TEA-butyl with 50 wt. % water at a fixed CO<sub>2</sub> loading of X<sub>CO2</sub>=0.48. This is about 60% lower than the comparative example of 30 wt. % monoethanolamine in water with the heat of absorption of approximately -80 kJ per mol of CO<sub>2</sub> at 40° C. Because the significantly lower heat of absorption for the ionic absorbent disclosed herein, the energy required to reverse the absorption reaction and release CO<sub>2</sub> in the solvent regeneration column is expected to decrease significantly.

#### EXAMPLE 8

Using the methods of Examples 6 and 7, the heat of absorption of TMA was calculated from experimental data. In the

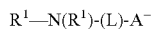
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temperature range of 40 to 80° C., the estimated heat of absorption was -63 kJ/mol, and in the range of 80 to 120° C. the estimated heat of absorption was -65 kJ/mol. The heat of absorption for 30 wt. % MEA also increases with temperature, and FIG. 10 is a plot of the heat of absorption of CO<sub>2</sub> in aqueous solutions of MEA and TMA as a function of temperature. The MEA data was from Kim et al., "Heat of Absorption of CO<sub>2</sub> in MEA and AEEA Solutions", Ind. Eng. Chem. Res., 46, (2007). The data for TMA were plotted at the midpoint of the temperature ranges above. It is clear from FIG. 10 that the heat of absorption for CO<sub>2</sub> in aqueous solutions of this amine-functionalized ionic liquid is significantly lower than that of MEA. Accordingly, this will reduce the energy requirement for liberating CO<sub>2</sub> from the CO<sub>2</sub>-rich solvent in the regenerator.

It will be understood that various modifications may be made to the embodiments disclosed herein. Therefore the above description should not be construed as limiting, but merely as exemplifications of embodiments. For example, the functions described above and implemented as the best mode for operating the present invention are for illustration purposes only. Other arrangements and methods may be implemented by those skilled in the art without departing from the scope and spirit of this invention. Moreover, those skilled in the art will envision other modifications within the scope and spirit of the claims appended hereto.

What is claimed is:

1. A method for improving the total energy demand required to separate carbon dioxide (CO<sub>2</sub>) from an aqueous ionic absorbent solution in a post-combustion carbon capture process, the method comprising (a) contacting a flue gas stream containing CO<sub>2</sub> with an aqueous ionic absorbent solution under absorption conditions to absorb at least a portion of the CO<sub>2</sub> from the flue gas stream and a CO<sub>2</sub>-aqueous ionic absorbent solution stream, wherein the aqueous ionic absorbent solution comprises about 25 wt. % to about 60 wt. % of one or more diluents, based on the total weight of the aqueous ionic absorbent solution, of one or more diluents and an ionic absorbent containing a cation and an anion comprising an amine moiety, wherein the cation comprises one or more cations selected from the group consisting of an ammonium cation, a phosphonium cation, a Group 1 metal cation and a Group 2 metal cation and the anion comprising an amine moiety is represented by the general formula:



wherein R<sup>1</sup> is the same or different and includes hydrogen, a straight or branched C<sub>1</sub> to C<sub>30</sub> substituted or unsubstituted alkyl group, a C<sub>1</sub> to C<sub>20</sub> ester-containing group, a substituted or unsubstituted C<sub>3</sub> to C<sub>30</sub> cycloalkyl group, a substituted or unsubstituted C<sub>3</sub> to C<sub>30</sub> cycloalkylalkyl group, a substituted or unsubstituted C<sub>3</sub> to C<sub>30</sub> cycloalkenyl group, a substituted or unsubstituted C<sub>5</sub> to C<sub>30</sub> aryl group, a substituted or unsubstituted C<sub>5</sub> to C<sub>30</sub> arylalkyl group, a substituted or unsubstituted C<sub>5</sub> to C<sub>30</sub> heteroaryl group, a substituted or unsubstituted C<sub>3</sub> to C<sub>30</sub> heterocyclic ring, a substituted or unsubstituted C<sub>4</sub> to C<sub>30</sub> heterocyclolalkyl group, a substituted or unsubstituted C<sub>6</sub> to C<sub>30</sub> heteroarylalkyl group, or R<sup>1</sup> and R<sup>1</sup> together with

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the nitrogen atom to which they are bonded are joined together to form a heterocyclic group; L is a linking group; and A<sup>-</sup> is an anionic moiety; and (b) subjecting at least a portion of the CO<sub>2</sub>-aqueous ionic absorbent solution stream to desorption conditions to form a CO<sub>2</sub>-rich stream and an aqueous ionic absorbent solution stream having a reduced CO<sub>2</sub> content, wherein the method reduces the total energy demand required to separate CO<sub>2</sub> from an aqueous ionic absorbent solution in a post combustion carbon capture process.

2. The method of claim 1, wherein the flue gas stream contains about 100% humidity.

3. The method of claim 1, wherein the one or more diluents comprise a diluent selected from the group consisting of a monohydric alcohol, a polyol and mixtures thereof.

4. The method of claim 1, wherein the cation comprises one or more of a secondary, tertiary or quaternary ammonium cation, or a secondary, tertiary or quaternary phosphonium cation.

5. The method of claim 1, wherein the cation has a molecular weight of about 18 to about 500 atomic mass unit (AMU).

6. The method of claim 1, wherein R<sup>1</sup> is the same or different and is a straight or branched C<sub>1</sub> to C<sub>6</sub> substituted or unsubstituted alkyl group, L is a divalent straight or branched C<sub>1</sub> to C<sub>6</sub> substituted or unsubstituted alkyl group and A<sup>-</sup> is SO<sub>3</sub><sup>-</sup>.

7. The method of claim 1, wherein the aqueous ionic absorbent solution comprises an ionic absorbent selected from the group consisting of tetrabutylammonium N-propyl-N-(3-sulfopropyl)amine, tetrabutylphosphonium N-isopropyl-N-(3-sulfopropyl)amine, tetraethylammonium N-isopropyl-N-(3-sulfopropyl)amine, tetramethylammonium N-isopropyl-N-(3-sulfopropyl)amine, tetramethyl ammonium N-propyl-N-(3-sulfopropyl)amine and mixtures thereof.

8. The method of claim 1, wherein the molecular weight of the ionic absorbent is from about 75 to about 700 atomic mass unit (AMU).

9. The method of claim 1, wherein the aqueous ionic absorbent solution has a viscosity of about 0.1 to about 100 centistokes (cSt).

10. The method of claim 1, wherein the absorption conditions include ambient pressure or a pressure of from 1.1 to about 1.5 bar, the gas stream has a temperature of about 80° C. to about 120° C. and the aqueous ionic absorbent solution has a temperature of about 20° C. to about 60° C.

11. The method of claim 1, wherein the desorption conditions include a pressure of about 1.9 bar to about 10 bar and heating the CO<sub>2</sub>-aqueous ionic absorbent solution stream to a temperature of about 90° C. to about 200° C.

12. The method of claim 1, wherein the desorption conditions include heating the CO<sub>2</sub>-aqueous ionic absorbent solution stream to a temperature of about 100° C. to about 200° C. under atmospheric or high-pressure conditions.

13. The method of claim 1, wherein the gas stream is an exhaust stream from a plant.

14. The method of claim 13, wherein the plant is a power plant that employs a carbon-based fuel source.

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